



**TREATMENT OF PERFLUORINATED COMPOUNDS AND  
NITROAROMATICS BY PHOTOCATALYSIS IN THE PRESENCE OF  
ULTRAVIOLET AND SOLAR LIGHT**

THESIS

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**DEPARTMENT OF THE AIR FORCE  
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***AIR FORCE INSTITUTE OF TECHNOLOGY***

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THESIS

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Mario H. Tellez, BS

Captain, USAF

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### Abstract

Nitroaromatic compounds (NACs) and perfluorinated compounds (PFCs) are two classes of water contaminants of DoD concern due to their risk to the environment, personnel, and mission. NACs are primarily used in modern explosives and are widely found throughout military ranges and training sites. PFCs are emerging contaminants used in many industrial and commercial processes and products to include aqueous film-forming foams which were used extensively by the military during firefighting and training operations from 1970 to late 1990s. This study investigated the potential of an innovative technology, photocatalytic oxidation, to effectively and energy efficiently treat NAC and PFC-contaminated water. Heterogeneous photocatalytic oxidation using Titanium dioxide ( $\text{TiO}_2$ ), which has been used as a photocatalyst to successfully treat pollutants in numerous studies over the last 20 years, was doped with silver to extend its photosensitivity. The silver-doped  $\text{TiO}_2$  (Ag- $\text{TiO}_2$ ) was also immobilized on a glass substrate. This eliminated the need to separate the  $\text{TiO}_2$  from the water after treatment, which is a big improvement over treatment approaches that rely on mixing the catalyst into the contaminated water and then having to remove the catalyst. Three model contaminants, 2,4-DNT, PFOA, and PFOS, were degraded using  $\text{TiO}_2$  and Ag- $\text{TiO}_2$  immobilized on glass slides under sunlight and UV light in atmospheric conditions and neutral pH levels. Results indicate 2,4-DNT degrades at different rates depending on the radiation source and PFOA/PFOS do not degrade. 2,4-DNT degraded 14% and 15% in the presence of Ag- $\text{TiO}_2$  and  $\text{TiO}_2$ , respectively, under sunlight after 8 hours. After 8 hours under UV light, 2,4-DNT degraded 13% and 29% in the presence of Ag- $\text{TiO}_2$  and  $\text{TiO}_2$ , respectively.

*To my wife and daughter*

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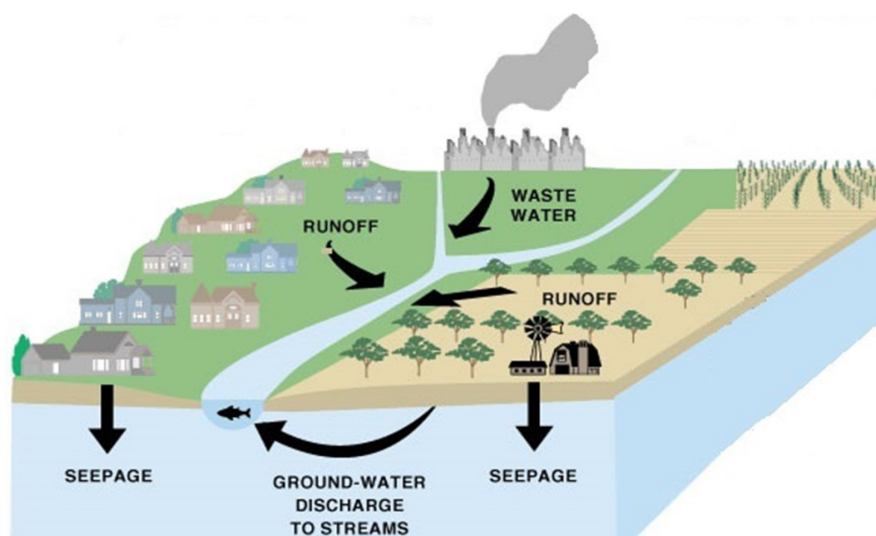
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# TREATMENT OF PERFLUORINATED COMPOUNDS AND NITROAROMATICS BY PHOTOCATALYSIS IN THE PRESENCE OF ULTRAVIOLET AND SOLAR LIGHT

## **I. Introduction**

### **Background**

Department of Defense (DoD) sites requiring environmental cleanup are contaminated by numerous types of compounds and contaminated in more than one medium. Surface and groundwater contamination affects many DoD sites. Contaminated surface and groundwater at DoD sites can enter the nation's aquifers, streams, rivers, and lakes which feed municipal, domestic, and agricultural water supplies, endangering public health and threatening the environment (Government Accounting Office, 2005). Additionally, the Government Accountability Office (2005) warns that contaminated water on DoD facilities "can pose a threat to military personnel, the public, and the sustainability of DoD's training and testing ranges." Water contamination primarily occurs through the direct discharge of hazardous substances from industrial, commercial, and residential sources directly into bodies of water, the transport of pollutants in storm water runoff, and the leaching of contaminated soil into the water table or bodies of water (see Figure 1) (Department of the Interior, 1998).



**Figure 1 - Sources of water contamination (Department of the Interior, 1998)**

This study focuses on effectively and energy efficiently treating Nitroaromatic Compounds (NACs) and Perfluorinated Compounds (PFCs), two classes of contaminants of DoD concern widely found at military ranges and training sites. According to the FY10 Defense Environmental Programs Annual Report to Congress, there are over 34,000 hazardous sites in DoD, with the Air Force having the greatest number of sites with groundwater contamination followed by the Navy and the Army (Government Accounting Office, 2005). Of these hazardous sites, approximately 2,300 are contaminated with munitions and contain NACs as a result of ammunition or explosive production, ammunition manufacturing, unexploded ordinance storage, and discarded military munitions (Department of Defense, 2010). Due to the emergent nature of PFCs, the DoD has only begun to systematically evaluate areas where possible sources of PFCs could be present, such as fire training areas that were operating between 1970 and 2000 (U.S. Air Force, 2012).

From 1995 to 2005, DoD invested approximately \$20 billion for environmental restoration of contaminated sites, including remediation of contaminated water on military installations (Government Accounting Office, 2005). Overall, DoD estimates the cost to restore all remaining sites to be \$28 billion (Department of Defense, 2010). An effective and energy efficient treatment method will save DoD restoration funds and expedite remediation efforts at its contaminated sites.

### **Perfluorinated Compounds**

PFCs are emerging contaminants that pose a potential risk to human health, DoD military operations, and the environment (Department of Defense, 2010). PFCs are a class of synthetic fluorinated chemicals whose unique physico-chemical characteristics make them very useful for a wide range of industrial and commercial application, such as non-stick polymers, water and stain proof coatings for paper and textiles, oxidative protective coatings on metals, inert surfactants for semi-conductor etching, aqueous film forming foams, and thermally stable lubricants (Lindstrom et al., 2011; Vecitis et al., 2009). PFCs' unique chemical properties make them persistent organic pollutants (Vecitis et al., 2009). Their persistent nature raises environmental and public health concerns as these compounds are toxic, extremely resistant to degradation, bioaccumulate in food chains, and can have long half-lives in humans (Richardson, 2007; Lindstrom et al., 2011). According to Appleman et al. (2013), certain PFCs are found in the serum of virtually all U.S. residents and have also been detected in the blood of wildlife in remote regions of the world. Additionally, PFCs are water soluble and have been detected in U.S. surface waters; including lakes, rivers, and tributaries, in the part per trillion ( $\text{ng L}^{-1}$ )

range or lower and have also been detected in surface and ground waters at similar concentrations (Appleman et al., 2013).

Two important classes of PFCs are perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) (Rahman et al., 2013). This study will specifically focus on one PFCA and one PFSA compound, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), respectively. The U.S. Environmental Protection Agency (EPA) classifies PFOA and PFOS, as “likely environmental carcinogens” (Environmental Protection Agency, 2009). In 2009, the EPA established Provisionary Health Advisory values for PFOA and PFOS of 0.4 and 0.2  $\mu\text{g L}^{-1}$ , respectively (Rahman et al., 2013). U.S. Air Force guidance classifies PFCs as emerging environmental contaminants based on “increasing regulatory interest, potential risk to human health, the environment, and evolving regulatory standards” (U.S. Air Force, 2012). In the 1970s, the Air Force began using Aqueous Film Forming Foam (AFFF) in fire-fighting training and operations, which contains PFOA and PFOS. Consequently, these contaminants have been found at DoD fire training sites where AFFF was used such as in in Wurtsmith Air Force Base in northeastern Michigan where PFC-based AFFF was used from 1950 until 1993. (Moody et al., 2003; Place & Field, 2012; Rak & Vogel, 2009).

DoD policy regarding emerging contaminants states that, “risks to people, the environment, and DoD missions, programs, and resources shall be assessed and, when appropriate, actions shall be taken to reduce risks related to emerging contaminants development, use, or release” (Department of Defense, 2009). Current Air Force interim policy is to “respond to validated human exposure to PFOS and PFOA with appropriate

interim action to mitigate exposures.” In 2011, the Air Force Center for Engineering and the Environment (now a component of the Air Force Civil Engineer Center) stated that there is a need to “develop innovative remedial strategies” to treat PFOS and PFOA (U.S. Air Force, 2012).

### **Nitroaromatic Compounds**

Nitroaromatic compounds (NACs) and their byproducts found at contaminated military sites present a potential hazard due to their explosive safety risks and potential toxicological effects (Stevens, 2004). The two most prevalent secondary explosives used by the U.S. military over the past 70 years are, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT). With their manufacturing impurities and environmental transformation products, RDX and TNT and their byproducts account for the majority of the explosives contamination at active military installations (U.S. Air Force, 2011).

NACs are a class of industrial chemicals found in numerous products, such as explosives, dyes, polyurethane foams, herbicides, pesticides and solvents (Phillips, 2003; Snellinx et al., 2002). Of the 2,300 DoD sites contaminated with NACs, a high percentage has groundwater contamination that is above permissible levels (Rodgers & Bunce, 2001). NACs’ susceptibility to leaching, due to their moderate water solubility, low volatility and extremely slow natural degradation makes them “among the most common groundwater and soil contaminants in the U.S., second only to the organochlorine functional group” (Environmental Protection Agency, 2012; Phillips, 2003; Reddy et al., 2011; Stevens, 2004). NACs, as well as their degradation byproducts, pose a significant danger to humans and the environment because of their toxicity,

mutagenicity and potential carcinogenicity. In fact, NACs' environmental transformation products, such as amines, are equally or more toxic than the parent nitroaromatic (Rodgers & Bunce, 2001). Due to their physico-chemical properties, NACs are recalcitrant to chemical and biological oxidation and to hydrolysis and can persist for many years in soil or groundwater (Phillips, 2003). Consequently, remediation of NAC-contaminated water is difficult (Rodgers & Bunce, 2001).

At many of the DoD munitions-contaminated sites, NACs such as TNT, RDX, and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrasocine (HMX), 2,4-Dinitrotoluene (2,4-drin) and others are the main contributors to water contamination (Stevens, 2004; Phillips, 2003). Due to laboratory safety issues associated with high energetics (i.e. TNT, HMX and RDX), this paper will use 2,4-DNT, a precursor to TNT, as the target NAC contaminant. According to Phillips (2003), under similar conditions, the transformation of 2,4-DNT is thought to be analogous to TNT, HMX and RDX degradation (Phillips, 2003).

The EPA identifies 2,4-DNT as a priority pollutant and is on its Drinking Water Contaminant Candidate List 2 for possible regulation under the Safe Drinking Water Act (Environmental Protection Agency, 2012). Among NACs, 2,4-DNT is the most toxic explosive compound as evidenced by its extremely low drinking water ( $0.11 \mu\text{g L}^{-1}$ ) and effluent discharge ( $0.7 \mu\text{g L}^{-1}$ ) limits set by the EPA (Mihás et al., 2007; Celin et al., 2003; Environmental Protection Agency, 2012). In 2006, the U.S. Air Force's Operational Range Assessment Plan identified operational ranges as essential to the mission of defending the United States and protecting its interests through air and space



power and listed 2,4-DNT and numerous other NACs as key contaminants at munition ranges that threaten human health and the environment (U.S. Air Force, 2011).

Consequently, in order to meet the Air Force commitment to sustaining its operational test and training ranges, innovative remedial strategies are needed to treat 2,4-DNT and other NACs.

### **Treatment Technologies**

Current methods to treat NAC-contaminated water sites involve the use of absorption, advanced oxidation processes (AOP), chemical reduction, and bioremediation (Snellinx et al., 2002). Methods to treat PFC-contaminated groundwater, however, are limited because of their unique physico-chemical properties and their only recent recognition as contaminants of concern (Vecitis et al., 2009).

Among the different treatment methods, AOP, and specifically heterogeneous photocatalytic oxidation utilizing modified nano-titanium dioxide ( $\text{TiO}_2$ ), is a promising method to effectively treat PFC- and NAC-contaminated water (Schmelling & Gray, 1995; Vecitis, et al., 2009).  $\text{TiO}_2$  is the most researched photocatalytic material “because it provides the most efficient photocatalytic activity, the highest stability, the lowest cost and the lowest toxicity” (Grabowska et al., 2012).  $\text{TiO}_2$ , however, requires ultraviolet (UV) radiation to activate its photocatalytic properties and since less than 5% of solar energy is emitted as UV radiation, using  $\text{TiO}_2$  on a large-scale application is limited (Swarnakar et al., 2013). A potential solution to this limitation is to extend  $\text{TiO}_2$  activation into the visible light region using catalyst doping agents. Based on previous research, metallic cation doping agents, specifically noble metals (e.g. silver,

gold) are effective in widening the TiO<sub>2</sub> light absorption range and promoting electrical conductivity (Daghrir et al., 2013).

Photocatalysis using TiO<sub>2</sub> has been applied to treat water contaminated with a variety of compounds (e.g., phenolics, chlorinated organics, herbicides, dyes, pharmaceuticals, etc.) (Gaya & Abdullah, 2008). Studies have also been accomplished using direct photolysis (solar and UV light) and photocatalysis (aqueous suspension of TiO<sub>2</sub> nanoparticles in UV light) to degrade PFOA, PFOS, 2,4-DNT and other NACs and PFCs. Mihas (2007) achieved full degradation of 2,4-DNT (1 mg L<sup>-1</sup>) when exposed to sunlight for 40 hours and achieved 57.8 % removal of 2,4-DNT when exposed to UV light for 4 hours (Mihas et al., 2007). The U.S. Navy reported 89% degradation of 2,6-DNT (154 mg L<sup>-1</sup>), a DNT isomer, dissolved in seawater under simulated solar radiation within 24 hours and full degradation after 72 hours (U.S. Navy, 2003). Dillert et al. (1995) reported 20% degradation of 2,6-DNT (18.2 mg L<sup>-1</sup>) in water under UV light using TiO<sub>2</sub> dispersed in aqueous solution in acidic conditions (pH = 3) after 10 minutes (Dillert et al., 1995). Nahen et al. (1997) reported greater than 99% TNT (54.6 mg L<sup>-1</sup>) removal within 60 minutes using TiO<sub>2</sub> dispersed in aqueous solution under UV light (Nahen et al., 1997). Schmelling et al. (1996) degraded TNT (50 mg L<sup>-1</sup>) more than 90% within 60 minutes in a TiO<sub>2</sub> slurry under near UV Light (>340 nm) (Schmelling & Gray, 1995). Finally, Wen et al. (2011) achieved 71% degradation of 2,4-DNT (50 mg L<sup>-1</sup>) in 60 hours under UV light alone and 77% degradation using a TiO<sub>2</sub> catalyst attached to a porous ceramic carrier in 60 hours (Wen et al., 2011). Table 1 shows previously reported rate constants for NACs under various conditions.

**Table 1 - Previously reported rate constants under various conditions**

Compound	Technique	Conditions	Degradation Rate (hr <sup>-1</sup> )	Reference
1,3,5-TNT	Dispersed TiO <sub>2</sub>	54.6 mg L <sup>-1</sup> UV (254 nm) pH = 9 O <sub>2</sub> , N <sub>2</sub>	6.3	Nahen et al. (1997)
1,3,5-TNT	Dispersed TiO <sub>2</sub>	50.0 mg L <sup>-1</sup> UV (340 nm) O <sub>2</sub>	4.7	Schmelling et al. (1995)
2,6-DNT	Sunlight	154.0 mg L <sup>-1</sup> (290-600 nm) Seawater	0.09	U.S. Navy (2003)
2,6-DNT	Dispersed TiO <sub>2</sub>	18.2 mg L <sup>-1</sup> UV (320 nm) pH = 3	1.5	Dillert et al. (1995)
2,4-DNT	Sunlight	1.0 mg L <sup>-1</sup> (290-600 nm) pH = 7	0.132	Mihas et al. (2007)
2,4-DNT	UV light	1.0 mg L <sup>-1</sup> (350-400 nm) pH = 7	0.185	Mihas et al. (2007)
2,4-DNT	Immobilized TiO <sub>2</sub>	50.0 mg L <sup>-1</sup> UV (254 nm) pH = 7	0.24	Wen et al. (2011)
PFOA	Simulated sunlight	41.1 mg L <sup>-1</sup> (290-600 nm) pH = 7	No degradation	Vecitus et al. (2009)
PFOA	UV light	41.1 mg L <sup>-1</sup> (254 nm) pH = 3.7	0.01	Chen et al. (2007)
PFOA	UV light	25.0 mg L <sup>-1</sup> (254 nm) pH = 7 O <sub>2</sub>	0.06	Wang and Zhang (2011)
PFOA	Dispersed TiO <sub>2</sub>	414.1 mg L <sup>-1</sup> UV (310-400 nm) pH = 2-3	0.06	Kutsuna et al. (2006)
PFOA	Dispersed TiO <sub>2</sub>	41.4 mg L <sup>-1</sup> UV (254 nm) pH = 3.8	0.06	Li et al. (2012)
PFOS	Simulated sunlight	50.0 mg L <sup>-1</sup> (290-600 nm) pH = 7	No degradation	Vecitus et al. (2009)
PFOS	UV light	20.0 mg L <sup>-1</sup> (254 nm) pH = 7 N <sub>2</sub>	0.0002	Yamamoto et al. (2007)

Vecitis et al. (2009) point out that direct photolysis in sunlight of PFOS and PFOA will be negligible in environmental conditions, reporting that PFOA ( $41.4 \text{ mg L}^{-1}$ ) and PFOS ( $50.0 \text{ mg L}^{-1}$ ) in aqueous solutions did not degrade in simulated sunlight for 30 days (Vecitis et al., 2009). However, PFOA in aqueous solution ( $41.4 \text{ mg L}^{-1}$ ) showed degradation under UV light resulting in a photolysis half-life of 24 hours, while PFOS, in similar conditions, has a slower degradation rate (half-life of 5.3 days) (Vecitis et al., 2009). Yuan et al. (2001) reported  $\text{TiO}_2$  photocatalytic degradation of PFOA resulted in 50% mineralization after 60 hours under UV light (Yuan et al., 2001). Wang et al. (2011) degraded PFOA using dispersed  $\text{TiO}_2$  in UV light in a oxygen atmosphere resulting in 12.4% degradation in 180 minutes (Wang et al., 2011). Chen et al. (2007) degraded PFOA ( $25 \text{ mg L}^{-1}$ ) under UV light (254 nm) resulting in 5% degradation after 120 minutes; however, when exposed to 184 nm UV light, PFOA degraded 60% within that time (Chen et al., 2007). Kutsuna et al. (2006) degraded PFOA ( $414 \text{ mg L}^{-1}$ ) by dispersed  $\text{TiO}_2$  under UV light and in acidic conditions (pH 2-3) resulting in a half-life of 1440 minutes (Kutsuna et al., 2006). Previously reported PFC rate constants under various conditions are shown in Table 1.

A review of the current literature indicates that studies using silver-doped  $\text{TiO}_2$  on solid glass substrates have not been used to treat 2,4-DNT, PFOA, or PFOS (Dillert et al., 2007; Gaya & Abdullah, 2008; Zhao & Zhang, 2009; Benotti et al., 2009; Estrellan et al., 2010; Grabowska et al., 2010; Swarnakar et al., 2013). While immobilization of the catalyst significantly lowers its efficiency compared to dispersion or slurries due to a reduction in catalyst surface area and poor mass transfer of reactants to the photocatalytic

surface, adhering the catalyst to a solid support enables industrial application by eliminating the majority of problems encountered with slurries and dispersion in aqueous solutions: (a) the need for separation or filtration steps, (b) the problematic use in continuous flow systems and (c) the particles aggregation, especially at high concentrations (Arabatzis et al., 2003; Byrne et al., 2011; Swarnakar et al., 2013).

### **Problem Statement**

The objective of this research is to explore the potential for  $\text{TiO}_2$  and Ag-doped  $\text{TiO}_2$  photocatalyst immobilized on glass substrates to effectively treat PFC-contaminated water and NAC-contaminated water under UV light and natural sunlight. The research questions to be answered in pursuit of this understanding are:

- What are the photocatalytic degradation rates for PFOS, PFOA and 2,4-DNT using undoped  $\text{TiO}_2$  as a catalyst, compared to using  $\text{TiO}_2$  doped with silver (Ag- $\text{TiO}_2$ ) as a catalyst?
- What is the difference between using UV light and natural solar light as energy sources for the photocatalytic treatment of PFOA, PFOS, and 2,4-DNT-contaminated water?
- What are the daughter products of PFOS, PFOA, and 2,4-DNT photodegradation?
- How does the composition of PFC and NAC degradation daughter products change over time during photodegradation?
- How may the kinetics of PFOS, PFOA, and 2,4-DNT degradation be modeled?

## **Methodology**

This research was conducted using batch-scale laboratory experiments. PFOS, PFOA and 2,4-DNT concentrations were measured over time under sunlight or UV light, and in the presence of undoped and Ag-doped TiO<sub>2</sub>. Experimental controls (i.e. contaminants exposed to solar or UV light only without the presence of TiO<sub>2</sub> or Ag-TiO<sub>2</sub> slides) will run concurrently to all experiments to assess the methods' effectiveness. Experimental results were also compared with the results of prior investigations using TiO<sub>2</sub> dispersed in a slurry solution and using UV light. Sample analysis was performed using gas chromatography-mass spectrometry, liquid chromatography-mass spectrometry, and ultraviolet-visible spectrophotometry techniques.

## **Assumptions/Limitations**

This study focused solely on PFC and NAC-contaminated water. External factors such as solution acidity and the laboratory environment were controlled, however uncontrolled external factors (i.e. temperature and solar radiation) affecting solar experiments that were run outside were statistically analyzed to determine their effect, if any, on experimental results.

## **Overview**

Chapter II will review existing literature on the photocatalysis of PFCs and NACs with a particular emphasis on the uses, properties and treatments of the target contaminants, details of the photocatalytic oxidation technology, and the potential photocatalytic degradation pathways of the target contaminants in the presence of TiO<sub>2</sub>.

and Ag-TiO<sub>2</sub>. Chapter III will detail the laboratory procedures and equipment used to gather the required quantitative data to explore the effectiveness of the proposed contaminated water treatment method. Chapter IV will present and analyze the experimental results. Finally, chapter V will present the conclusions of this study and propose areas for further investigation.

## **II. Literature Review**

This chapter discusses literature relevant to this study: to explore the potential for modified TiO<sub>2</sub> coated films on glass substrates doped with silver, to be used to treat PFC-contaminated water and NAC-contaminated water by photocatalysis in the presence of UV light and natural sunlight. The literature review researches PFC and NAC uses, properties, treatment technologies and degradation pathways.

### **Uses of Nitroaromatic Compounds**

NACs are a group of compounds widely found in commercial products (e.g., insecticides, herbicides, pharmaceuticals, dyes, plastics) and used extensively in industrial processes (Phillips, 2003). NACs, to include 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), dinitrotoluene (2,4-DNT and 2,6-DNT), dinitrobenzene (DNB), methyl-N,2,4,6-tetranitroaniline (Tetryl), and 2,4,6-trinitrophenol (picric acid), are principally used in the modern explosives industry (Rodgers & Bunce, 2001). According to Dutta et al. (2003), manufacturers in the U.S. generate millions of tons of TNT, DNT and toluene, a precursor to poly nitroaromatic compounds, annually (Dutta et al., 2003). TNT, in particular, was once the world's most widely used explosive, with 2 million pounds produced annually as of 1985 (Stevens, 2004).

Due to the extensive manufacture, use, improper handling and disposal of TNT, DNT, a primary intermediate product, has being found extensively in soil and groundwater contamination (Snellinx et al., 2002; Wen et al., 2011). Mohanty and Wei



(1993) report that in 1982 over 500 million pounds of DNT were produced (Mohanty & Wei, 1993). DNT is a poly-nitroaromatic compound not found naturally in the environment. DNT consists of six isomers (2,4-DNT, 2,6-DNT, 2,3-DNT, 2,5-DNT, 3,4-DNT, and 3,5-DNT) of which 2,4-DNT and 2,6-DNT make up 95 percent of technical grade DNT (Department of Health and Human Services, 2013).

### Properties of Nitroaromatic Compounds

As noted earlier, NACs are primarily used in modern explosives and thus found as contaminants throughout the DoD (Phillips, 2003). Within this group of NACs, of interest are (poly) nitrotoluenes that consist of a toluene molecule with several nitro ( $\text{NO}_2$ ) groups (Stevens, 2004). Figure 2 illustrates the nitration of toluene to form TNT as well as the immediate precursors (i.e. 2,4-DNT and 2,6-DNT).

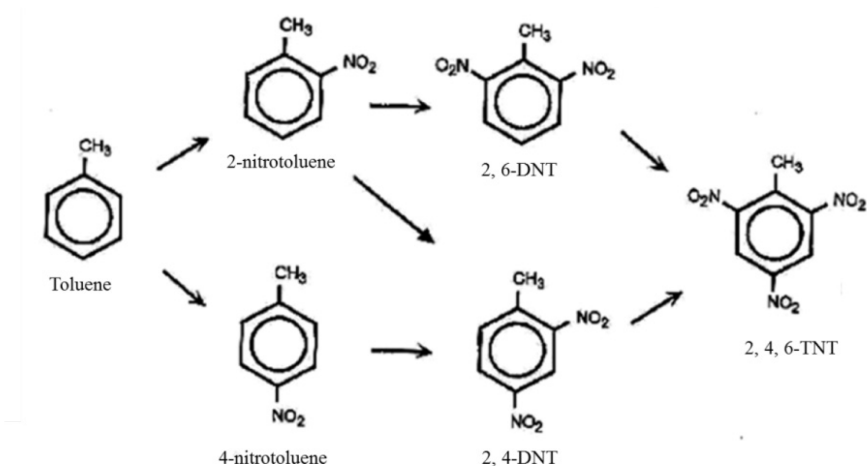


Figure 2 - Nitration of Toluene (Phillips, 2003)

The stability of explosive NACs is attributed to the electron-withdrawing nitro groups which become more stable as the number of nitro groups surrounding the benzene

ring increases (Rodgers & Bunce, 2001). 2,4-DNT, a pale yellow solid, has relatively low volatility (Henry's law constant =  $8.79 \times 10^{-8} \text{ atm m}^3 \text{ mol}^{-1}$ ) and is moderately soluble in water ( $270 \text{ mg L}^{-1}$ ) allowing it to be easily transported in surface or groundwater and to persist in the environment (See Table 2). Additionally, based on its relatively low organic-carbon partition coefficient ( $\log K_{OC} = 1.65$ ) and low octanol/water partition coefficient ( $\log K_{OW} = 1.98$ ), 2,4-DNT only has a slight tendency to adsorb to sediments or suspended solids. A case study investigated an old effluent lagoon that still contained detectable quantities of 2,4-DNT 12 years after it was retired (Department of Health and Human Services, 1998). Consequently, unless 2,4-DNT is broken down by light, oxygen or biota, it is expected to remain in the hydrological environment for long periods of time (Environmental Protection Agency, 2012).

**Table 2 - Physical and chemical properties of 2,4-DNT (Environmental Protection Agency, 2012)**

Property	2,4-DNT
Chemical Abstracts Service (CAS) Number	121-14-2
Physical Description (physical state at room temperature and atmospheric pressure)	Yellow solid
Molecular weight (g/mol)	182.14
Water solubility (mg/L at 22°C)	270
Melting Point (°C)	71
Boiling point (°C)	300 (slight decomposition)
Vapor pressure at 22 °C (mm Hg)	$1.47 \times 10^{-4}$
Specific gravity/Density	1.32 @ 71 °C
Octanol-water partition coefficient ( $\log K_{ow}$ )	1.98
Organic-carbon partition coefficient ( $\log K_{oc}$ )	1.65
Henry's law constant ( $\text{atm m}^3/\text{mol}$ )	$8.79 \times 10^{-8}$

Notes: g/mol – grams per mole; mg/L – milligrams per liter; °C – degree Celsius; mm Hg – millimeters of mercury;  $\text{atm m}^3/\text{mol}$  – atmosphere-cubic meters per mole.

## Treatment of Nitroaromatic Compounds

Numerous remediation techniques exist to treat NAC-contaminated water. The most relevant remediation techniques are adsorption, advanced oxidation processes

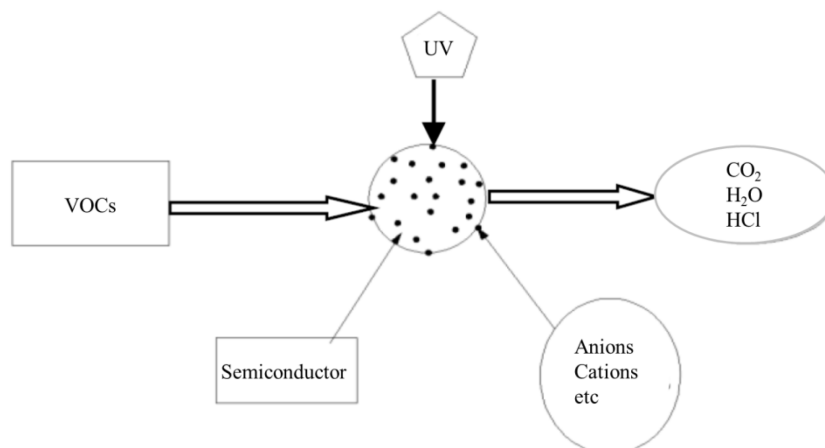
(AOPs), chemical reduction and bioremediation (Rodgers & Bunce, 2001). While the application of remediation techniques are highly dependent on the quantities and toxicity of the target NACs, adsorption on granular activated carbon (GAC) has been the most common treatment due to its simplicity and effectiveness (Phillips, 2003). This method, however, only transfers NACs from one medium to another and does not neutralize the pollutants. As such, the spent GAC must be treated or disposed of as hazardous waste, resulting in secondary environmental impacts (Government Accounting Office, 2005). The Department of Health and Human Services prescribes controlled incineration in an incinerator unit equipped with alkaline scrubbers as the ultimate disposal method of 2,4-DNT (Department of Health and Human Services, 2013).

AOP remediation is proving to be a good alternative for removing xenobiotic recalcitrant compounds, such as NACs, from polluted water (Mboula et al., 2013). AOPs principally work through the formation of hydroxyl radicals ( $\bullet\text{OH}$ ), a very reactive species, in water to quickly and non-selectively oxidize a wide range of organic compounds (Konstantinou & Albanis, 2004). Among AOPs, the most promising are heterogeneous photocatalytic reactions with semiconductors, which, are initiated when a semiconductor (SC) is irradiated by photons,  $h\nu$ , that equal or exceed the semiconductor's band gap to promote electrons from the valence band to the conduction band and concurrently producing positively charged holes (Gaya & Abdullah, 2008; Konstantinou & Albanis, 2004; Prieto-Rodriguez et al., 2012). The following reactions (Equations 1-4) have been widely postulated (Gaya & Abdullah, 2008):

<b>Equation 1</b>	<b>Photexcitation:</b>	$SC + h\nu \rightarrow e^- + h^+$
<b>Equation 2</b>	<b>Oxygen ionosorption:</b>	$(O_2)_{ads} + e^- \rightarrow O_2^{\cdot -}$
<b>Equation 3</b>	<b>Ionization of water:</b>	$H_2O + h^+ \rightarrow \bullet OH + H^+$
<b>Equation 4</b>	<b>Protonation of superoxides:</b>	$O_2^{\cdot -} + H^+ \rightarrow HOO^{\cdot}$

Both oxidative and reductive reactions can occur on the surface of the semiconductor, where the organic pollutants are adsorbed (Liang et al., 2012).

Heterogeneous photocatalysis, unlike GAC, breaks down organic pollutants from complex molecules to simple and non-hazardous substances without producing waste needing secondary treatment or disposal (see Figure 3) (Kaan et al., 2012). However, despite the promise of AOPs, there are two major drawbacks that must be addressed to make them a competitive alternative to GAC. First, AOPs are energy intensive requiring an artificial ultraviolet (UV) light source to produce the required energy to exceed the semiconductors' band gap energy and produce the electron ( $e^-$ ) and electron holes ( $h^+$ ) that begin to generate the photocatalytic reaction. Second, and perhaps most significant, is the tendency for the fast recombination of the newly generated electron/holes to recombine before reacting with the organic contaminants and their intermediates products (Daghrir et al., 2013). These drawbacks will be addressed in the subsequent section.



**Figure 3 - Decomposition path of volatile organic compounds (VOCs) in heterogeneous photocatalytic oxidation under UV light (Liang et al., 2012)**

### Uses of Perfluorinated Compounds

PFCs are a group of chemicals used extensively in the manufacturing of a wide variety of industrial (e.g. protective sprays, waxes, semiconductors, fire-fighting foams) and consumer products (e.g. non-stick cookware, masking tape, food packaging, treated carpets, upholstery, and clothing) due to their unique physico-chemical properties such as extremely high thermal and chemical stability (Appleman et al., 2013; Rahman et al., 2013). Introduced in the 1950s, PFCs have become ubiquitous as their use in industrial and consumer products has expanded. Perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs), both consisting of a fluorinated carbon backbone and either a carboxyl group or a sulfonic group, respectively, are the most environmentally relevant PFCs (Department of Health and Human Services, 2009; Place & Field, 2012). According to the Department of Health and Human Services, PFOA and PFOS are the most significant compounds within these groups as they are made in the

largest amounts in the United States; between 15,000 and 500,000 pounds of PFOA and PFOS were produced during 2002 (Department of Health and Human Services, 2009).

Due to their ubiquity and their health and environmental effects, PFOA and PFOS are being voluntarily phased out by eight major U.S. manufacturers with a goal of eliminating emissions and product content by 2015 (Place & Field, 2012). This phase-out has led to the increasing use of shorter chain length PFCs which are less ecologically toxic (Post et al., 2012). In spite of the voluntary phase-out of PFOA and PFOS, large stockpiles of materials containing PFOA and PFOS still exist. One specific stockpiled material is aqueous film-forming foams (AFFF), whose repeated use during fire training operations has been correlated to higher concentrations to PFOA and PFOS levels in surface water and groundwater in the surrounding environment (Place & Field, 2012). According to Place and Field (2012), in 2004 the U.S. maintained a stockpile of approximately 38 million liters of AFFF with no restrictions or regulations in place regulating its use or disposal (Place & Field, 2012). PFOA and PFOS are of particular interest to the Air Force and Department of Defense, who possess the largest stockpile (approximately 11 million liters) of AFFF and have used PFC-based AFFF since the 1970s, releasing directly into the environment after use (Place & Field, 2012; U.S. Air Force, 2012).

### **Properties of Perfluorinated Compounds**

As previously noted, PFCs are found in a wide-ranging number of commercial and industrial products, from non-stick cookware to protective coatings on metals and in AFFF (Vecitis et al., 2009). PFCs' chemical properties allow their use in varying and

sometimes harsh conditions requiring high thermal and chemical stability (Estrellan et al., 2010). These chemical properties, however, also makes them particularly recalcitrant, environmentally persistent and resistant to conventional treatment methods. The chemical structure of PFCs includes a completely fluorinated carbon chain (ranging from 4 to 13 carbons), which is both hydrophobic and oleophobic, and a hydrophilic charged functional group (carboxylic or sulfonic acid) (Estrellan et al., 2010; Post et al., 2012). Figure 4 shows the structure and chemical properties of selected PFCs (Rahman et al., 2013). The substitution of Hydrogen with Fluorine atoms gives PFCs their high thermal and chemical stability, as C-F bonds are one of the strongest bonds found in nature (Richardson, 2007). According to Vecitis et al. (2009), fluorine's high reduction potential ( $E^0 = 3.6 \text{ V}$ ) makes it thermodynamically unfavorable to create a bond with any other one-electron oxidant (Vecitis et al., 2009). Additionally, the perfluorinated tail, when properly oriented, make PFCs ideal surfactants and dispersants such as firefighting foams (Lindstrom et al., 2011)

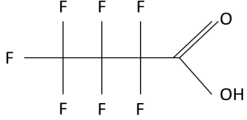
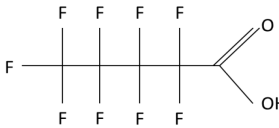
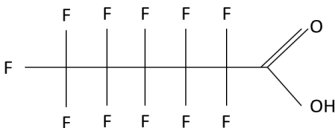
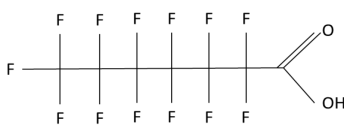
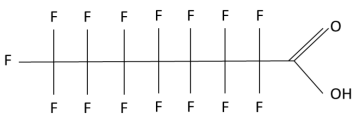
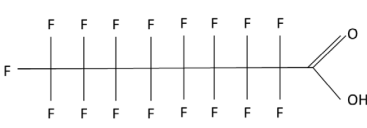
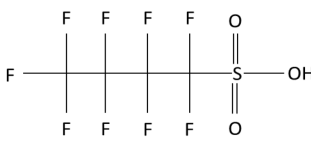
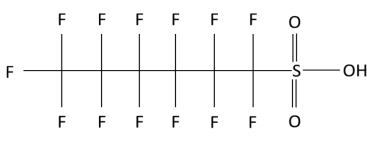
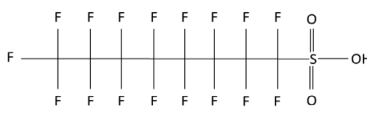
Compound Name	Structure
Perfluorobutanoic acid (PFBA)	
Perfluoropentanoic acid (PFPeA)	
Perfluorohexanoic acid (PFHxA)	
Perfluoroheptanoic acid (PFHpA)	
Perfluorooctanoic acid (PFOA)	
Perfluorononanoic acid (PFNA)	
Perfluorobutane sulfonic acid (PFBS)	
Perfluorohexane sulfonic acid (PFHxS)	
Perfluorooctane sulfonic acid (PFOS)	

Figure 4 - Structure and physico-chemical properties of selected PFCs (Rahman et al., 2013)



PFOA and PFOS are of particular concern due to their high production volumes, and pervasiveness in the environment (Estrellan et al., 2010; Rahman et al., 2013).

PFOA consists of a fully fluorinated seven carbon chain with a carboxylic headgroup and PFOS consists of a fully fluorinated eight carbon chain with a sulfonic headgroup.

According to Liu et al. (2004), increasing the fluorinated carbon chain length makes the PFC compound more inert by reducing the oxidizability of the ionic headgroup ( $\text{SO}_3^-$  for PFOS and  $\text{CO}_2^-$  for PFOA) since it inductively reduces headgroup electron density (Liu et al., 2004). Table 3 shows the physical and chemical properties of PFOA and PFOS (Environmental Protection Agency, 2009). The acidic nature (i.e. low acid dissociation constants ( $\text{pK}_a = -3$  to 4) of PFOS and PFOA indicate that they predominantly exist in anionic form in the environment. The anionic form indicates that they are chemically stable and have low volatility allowing them to readily migrate from soil to water.

Additionally, due to their longer chain length, PFOA and PFOS, have a high tendency to bind to organic matter and thus bioaccumulate (Environmental Protection Agency, 2009).

**Table 3 - Physico-chemical properties of PFOA and PFOS (Environmental Protection Agency, 2009)**

Property	PFOA	PFOS (Potassium Salt)
Chemical Abstracts Service (CAS) Number	335-67-1	2795-39-3
Physical Description (physical state at room temperature and atmospheric pressure)	White powder/waxy white solid	White powder
Molecular weight (g/mol)	414	538 (potassium salt)
Water solubility (mg/L at 22°C)	9.5 X 10 <sup>3</sup> (purified)	570 (purified), 370 (freshwater), 25 (filtered seawater)
Melting Point (°C)	45 to 50	> 400
Boiling point (°C)	188	Not measurable
Vapor pressure at 22 °C (mm Hg)	0.017	2.48 X10 <sup>-6</sup>
Air water partition coefficient (Pa.m <sup>3</sup> /mol)	Not available	< 2 X10 <sup>-6</sup>
Octanol-water partition coefficient (log K <sub>ow</sub> )	Not measurable	Not measurable
Organic-carbon partition coefficient (log K <sub>oc</sub> )	2.06	2.57
Henry's law constant (atm m <sup>3</sup> /mol)	Not measurable	3.05 × 10 <sup>-9</sup>
Half-Life	Atmospheric: 90 days; Water: > 92 years (at 25°C)	Atmospheric: 114 days; Water: > 41 years (at 25° C)

Notes: g/mol – grams per mole; mg/L – milligrams per liter; °C – degree Celsius; mm Hg – millimeters of mercury; atm m<sup>3</sup>/mol – atmosphere-cubic meters per mole.

## Treatment of Perfluorinated Compounds

Despite their long use, PFCs have only in the last 25 years become a concern to the environment and human health. PFCs emergence as a significant ecological pollutant stems from recent advances in chromatographic technology in the late-1990s allowing for the first time to determine, analyze and characterize very low concentration background levels (ng mL<sup>-1</sup> range) (Lindstrom et al., 2011; Pobozy et al., 2011). Due to the only recent recognition of PFCs as contaminants of concern, their very low environmental concentrations, and their unique physio-chemical properties, as discussed previously, limited effective treatment technologies exist (Vecitis et al., 2009). Studies indicate that natural environmental degradation processes and conventional treatment methods have little to no effect on PFC degradation. A study of PFOS levels at a former fire-training site at Wurtsmith Air Force Base in northeastern Michigan by Moody et al (2003) found PFOS and PFOA-contaminated groundwater at levels 20 to 500 times higher than the EPA Provisionary Health Advisory levels ten years after the end of fire training activities,

indicating the compounds' resistance to environmental degradation (Moody et al., 2003; Environmental Protection Agency, 2009). Similarly, Rahman et al. (2013) indicate that PFOA and PFOS are not susceptible to microbial degradation as these compounds do not seem to be used as carbon sources (Rahman et al., 2013).

While optimal PFC treatment techniques are highly dependent on contaminant initial concentration, available degradation time, background organic and metal concentration, and other site-specific conditions, currently the most effective and utilized treatment technique for removing PFCs, and specifically PFOA and PFOS, is granular activated carbon (GAC). However, an inherent drawback with GAC is the need to dispose of the secondary waste (i.e. spent GAC) through costly controlled incineration (Environmental Protection Agency, 2009). Other treatment technologies for PFC-contaminated water include sonochemical degradation, chemical reduction, and advanced oxidation process (AOPs) (Vecitis et al., 2009).

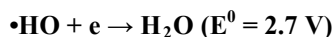
It has been reported that sonochemical methods can efficiently degrade PFCs (Appleman et al., 2013; Li et al., 2012). The effectiveness of sonochemical degradation is attributed to the cavitation bubbles created by the ultrasound waves. Moriwaki et al. (2005) indicate that organic pollutants degrade via reactions with hydroxyl radicals formed by the cavitation bubbles and via direct pyrolysis reaction inside and in the vicinity of the collapsing bubble (Moriwaki et al., 2005). Moriwaki et al. (2005) reported a half-life of 43 and 22 minutes for PFOS and PFOA, respectively, using sonochemical degradation (Moriwaki et al., 2005). Cheng et al. (2010) investigated sonochemical degradation of PFOA and PFOS in groundwater samples and reported a 97% and 80%

decrease in concentration at 120 minutes, respectively (Cheng et al., 2010).

Sonochemical degradation is the only technique that can quickly degrade PFOS and PFOA; however the method requires energy to produce the ultrasound waves, is limited to batch systems due to the relatively high residence time needed for substantial degradation, and degradation rates are reduced in organic-rich water (Vecitis et al., 2009; Cheng et al., 2010).

An alternative remediation technique of interest is AOP, and more specifically heterogeneous photocatalytic reactions with semiconductors. An overview of the literature indicates low effectiveness of AOPs in the destruction of PFCs, particularly long chained compounds such as PFOA and PFOS due to their high thermal and chemical stability (Estrellan et al., 2010; Department of Health and Human Services, 2009; Dillert et al., 2007; Li et al., 2012; Liu et al., 2004; Vecitis et al., 2009; Zhao & Zhang, 2009). The relative ineffectiveness of heterogeneous photocatalysts in degrading PFCs is mainly attributed to the inability of hydroxyl radicals ( $\bullet\text{OH}$ ) to withdraw hydrogen atoms from PFCs, specifically the PFCs PFOA and PFOS, to form water since all the hydrogen atoms in PFCs have been replaced with fluorine atoms (Rahman et al., 2013). Hydroxyl radicals are also prevented from abstracting hydrogen atoms from the relatively neutral pH levels in the environment (Liu et al., 2004). Dillert et al. (2006) reported the degradation of numerous PFCs under UV light in the presence of dispersed  $\text{TiO}_2$  only under highly acidic conditions ( $\text{pH} = 1$ ) (Dillert et al., 2007). Consequently, the hydroxyl radical must act through direct electron transfer to form the less reactive species, hydroxyl ion (See Equations 5 & 6) (Vecitis et al., 2009).

**Equation 5**



**Equation 6**



Despite the widely reported ineffectiveness of heterogeneous photocatalysts to degrade PFCs, several reports indicate the possibility of degrading PFCs using this method. Li et al. (2012) investigated the heterogeneous photocatalytic decomposition of PFOA by dispersed indium oxide ( $\text{In}_2\text{O}_3$ ) and dispersed  $\text{TiO}_2$  under UV light (254 nm) and reported 80% and 15.9% decrease, respectively, within 4 hours (Li et al., 2012). Additionally, Wang & Zhang (2011) investigated the decomposition of PFOA in aqueous solution by dispersed  $\text{TiO}_2$  under UV light at varying pH levels and atmospheres (i.e. nitrogen and oxygen) and reported PFOA (at pH = 7) decomposing 10.5% and 12.4% under an oxygen and nitrogen atmosphere, respectively, within 180 minutes. Of note is the reported 86.7% decomposition of PFOA (at pH = 2.47) after 180 minutes (Wang & Zhang, 2011).

These results indicate the possibility of successfully degrading PFCs, specifically PFOA and PFOS, using heterogeneous photocatalytic decomposition with a cheap, safe and abundant semiconductor (i.e.  $\text{TiO}_2$ ) at an environmentally relevant pH. Ideally, it would be possible to achieve degradation rates comparable to those achieved above at low pH, by treatment with a low energy source such as solar light, and using an immobilized catalyst which would not need to be separated from the water after treatment. immobilized catalyst which would not need to be separated from the water after treatment.

## Photocatalysis Using TiO<sub>2</sub>

Heterogeneous photocatalysis using TiO<sub>2</sub> as a catalyst is emerging as one of the most effective and efficient technologies to photo-mineralize organic pollutants into simple molecules such as CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and halide ions (Gaya & Abdullah, 2008; Konstantinou & Albanis, 2004). It has been reported that of the various semiconductors used in environmental applications, such as WO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SrTiO<sub>3</sub>, ZnO, CeO<sub>2</sub>, CdS, and ZnS, TiO<sub>2</sub> has the best photocatalytic performance with maximum quantum yields (Herrmann, 1999; Tseng et al., 2010). The use of TiO<sub>2</sub> as a semiconductor in heterogeneous photocatalytic reactions has several other advantages: TiO<sub>2</sub> is abundant, relatively inexpensive, environmentally benign during degradation, operates at ambient temperature and pressure, resists photo-corrosion and has a favorable band-gap energy (Kwon et al., 2008; Liang et al., 2012). Estimated worldwide reserves of TiO<sub>2</sub> are in excess of 600 million tons and the annual production of TiO<sub>2</sub> is approximately 4.3 million tons (Daghrir et al., 2013). TiO<sub>2</sub>'s low energy band gap, which ranges from 3.0-3.2 eV depending on the crystalline structure, makes it more attractive than other leading semiconductors, such as ZnO (3.35 eV) and SnO<sub>2</sub> (3.6 eV) (Teh & Mohamed, 2011).

There are three different types of TiO<sub>2</sub> (anatase, rutile and brookite) each with their unique crystal structures (Teh & Mohamed, 2011). While rutile is the most common form of TiO<sub>2</sub>, it has been reported that the open crystalline structure of anatase allows for the best photocatalytic activity and thus the most practical for widespread environmental applications (Kaan et al., 2012; Kwon et al., 2008). Figure 5 shows the primary processes involved in photomineralizing organic compounds. Table 4 lists the

elementary mechanisms of photocatalytic degradation of organic compounds by  $\text{TiO}_2$  catalysis and the characteristic times for each reaction (Gaya & Abdullah, 2008).

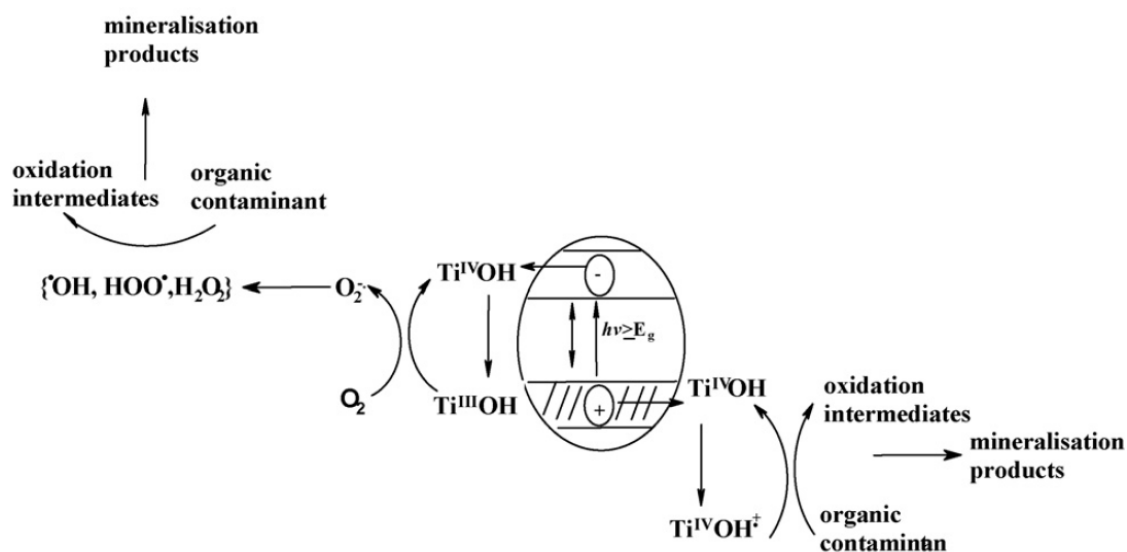


Figure 5 - Primary process involved in photomineralization of organic compounds by  $\text{TiO}_2$  (Gaya & Abdullah, 2008)

**Table 4 - Primary processes and characteristic reaction times for mineralization of organic pollutants by TiO<sub>2</sub> (Gaya & Abdullah, 2008)**

Primary process	Characteristic time
Charge carrier generation $\text{TiO}_2 + h\nu \rightarrow e^- + h^+$	fs (very fast)
Charge carrier trapping $h^+ + >\text{Ti}^{\text{IV}}\text{OH} \rightarrow \{>\text{Ti}^{\text{IV}}\text{OH}^{*+}\}$ $e^- + >\text{Ti}^{\text{IV}}\text{OH} \rightleftharpoons >\text{TiOH}^{\text{III}}\}$	10 ns (fast) 100 ps (shallow trap; dynamic equilibrium)
$e^- + >\text{Ti}^{\text{IV}} \rightarrow \text{Ti}^{\text{III}}$	10 ns (deep trap)
Charge carrier recombination $e^- + \{>\text{Ti}^{\text{IV}}\text{OH}^{*+}\} \rightarrow >\text{Ti}^{\text{IV}}\text{OH}$ $h^+ + >\text{Ti}^{\text{III}}\text{OH} \rightarrow \text{Ti}^{\text{IV}}\text{OH}$	100 ns (slow) 10 ns (fast)
Interfacial charge transfer $\{>\text{Ti}^{\text{IV}}\text{OH}^{*+}\} + \text{organic molecule} \rightarrow >\text{Ti}^{\text{IV}}\text{OH} + \text{oxidized molecule}$ $\{>\text{Ti}^{\text{III}}\text{OH}\} + \text{O}_2 \rightarrow >\text{Ti}^{\text{IV}}\text{OH} + \text{O}_2^{*-}$	100 ns (slow) ms (very slow)

As previously mentioned, heterogeneous photocatalytic reactions with semiconductors, using TiO<sub>2</sub>, require sufficient light intensity to meet or exceed the energy band gap of the semiconductor in order to generate the photocatalytic reaction (see Figure 6) (Swarnakar et al., 2013). In the case of anatase TiO<sub>2</sub> a wavelength of 387 nm is required to meet or exceed its energy band gap of 3.2 eV (Tseng et al., 2010). Thus, the required wavelength falls in the upper limit of UV radiation (200-400 nm), more specifically the UVA domain (320-400 nm) (Byrne et al., 2011). As a result, heterogeneous photocatalytic reactions must occur in artificial UV light as all of the high energy UV domains (UVC - 200-280 nm and UVB - 280-320 nm) in natural sunlight are absorbed by the atmospheric ozone and therefore natural sunlight only consists of 3-5% UVA light (Byrne et al., 2011; Swarnakar et al., 2013; Teh & Mohamed, 2011). Consequently, unless mitigated, heterogeneous photocatalysis' dependence on high-energy UV light limits its commercial potential (Tseng et al., 2010).



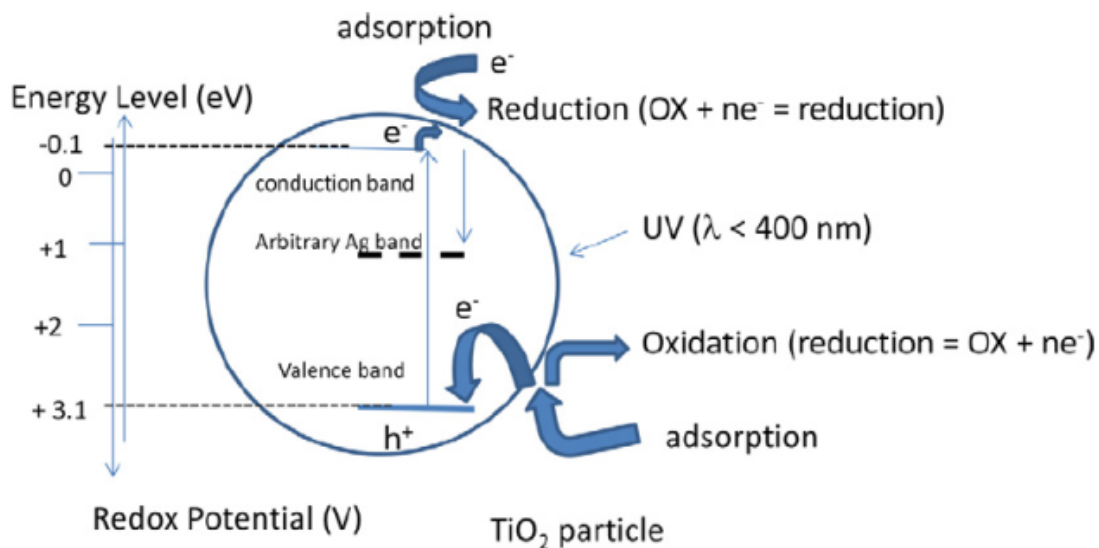


Figure 6 - Schematic diagram of the photocatalytic mechanism of Ag doped TiO<sub>2</sub> film (Swarnakar et al., 2013)

In order to ensure heterogeneous photocatalysis, and photocatalysis with TiO<sub>2</sub> specifically, is a viable alternative to GAC and other remediation techniques, sensitizing the semiconductor to visible light is of great importance in order to mitigate its dependence on UV radiation and be able to effectively use natural sun light as an energy source to generate the photocatalytic reactions (Teh & Mohamed, 2011). Numerous studies have focused on elevating the photocatalytic activity of TiO<sub>2</sub> using metals and nonmetals as doping agents.

Doping of TiO<sub>2</sub> with nonmetals, such as C, N, S, P, B, P, I and F has shown to significantly improve the photosensitivity of TiO<sub>2</sub> (Tseng et al., 2010). Asahi et al. (2001) assessed the capability of several nonmetal doping agents (i.e. C, N, F, P and S) to produce states in the band gap that absorb visible light. They reported that N doping was

the most effective due to the mixing of its  $p$  orbitals with the oxygen  $2p$  orbitals (Asahi et al., 2012). Daghrir et al. (2013) similarly assessed several nonmetals as doping agents to extend  $\text{TiO}_2$ 's sensitivity into the visible spectrum and reported nitrogen and carbon as being the most effective in ensuring higher photocatalytic activity of  $\text{TiO}_2$  under visible light (Daghrir et al., 2013). Despite the promise of doping  $\text{TiO}_2$  with nonmetals, several disadvantages have been reported such as a decrease of dopant during the annealing process and, ultimately, that the photocatalytic activity under visible light of nonmetal-doped  $\text{TiO}_2$  is much lower than under UV light (Han et al., 2011; Teh & Mohamed, 2011; Zaleska, 2008).

Doping of  $\text{TiO}_2$  with metals (transition, rare earth and noble metals) has generally widened the light absorption range of  $\text{TiO}_2$  into the visible light spectrum (Teh & Mohamed, 2011). Daghrir et al. (2013) cautions that doping with metal may cause defects that can decrease the photocatalytic activity due to the creation of recombination centers for the electrons/holes; however, he states that the defects can be avoided by re-annealing the doped  $\text{TiO}_2$  (Daghrir et al., 2013). Recently noble metals, such as Ag, Pt, Au, Pd, Os, Ir, Ru, and Rh have gained interest due to their high resistance to oxidation in aqueous environments as compared to other metals. These noble metals have been reported to serve as light absorbing sensitizers and as centers of charge separation, thus increasing the photocatalytic effectiveness of  $\text{TiO}_2$  (Daghrir et al., 2013; Grabowska et al., 2010; Teh & Mohamed, 2011).

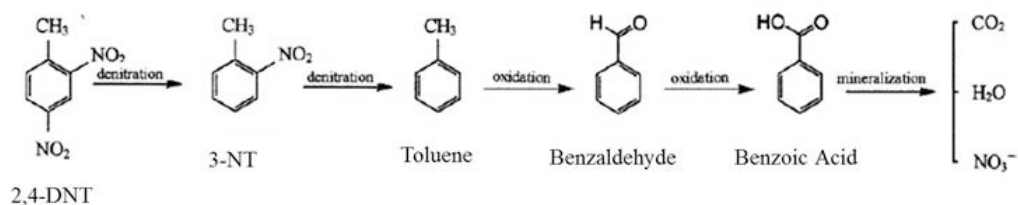
Silver-doped  $\text{TiO}_2$  (Ag- $\text{TiO}_2$ ), in particular, has been of considerable interest due to its effectiveness in extending  $\text{TiO}_2$  absorption into the visible spectrum, aiding

electron-hole separation through oxygen adsorption and increasing the  $\text{TiO}_2$ 's specific surface area, thus providing more sites for photoreactions (Arabatzis et al., 2003; Mboula et al., 2013; Teh & Mohamed, 2011). While it has been reported that platinum's photocatalytic activity is greater than silver's, silver's low cost and easier preparation makes it the most suitable photocatalyst for commercial applications (Liu et al., 2004). Additionally, Grabowska et al. (2010) reported that silver enables the increase of photocatalytic activity both under UV light and visible light, and Castro et al. (2011) reported that silver-doped  $\text{TiO}_2$  extends the absorption to wavelengths up to 600 nm (Castro et al., 2012; Grabowska et al., 2010). Under UV irradiation, silver deposits act as electron traps, thus leading to the enhancement of Ag- $\text{TiO}_2$  photocatalytic activity (Sobana et al., 2006). Numerous studies have reported increased rates of degradation for a wide range of pollutants, to include rhodamine 6G dye, methylene blue, methyl orange, phenol, Cr (IV), direct diazo dyes, short chain carboxylic acids, and toluene when using Ag- $\text{TiO}_2$  as a photocatalyst (Daghrir et al., 2013; Liang et al., 2012; Liga et al., 2011; Liu et al., 2004; Sobana et al., 2006).

## **2,4-DNT Degradation Pathways in the Presence of $\text{TiO}_2$**

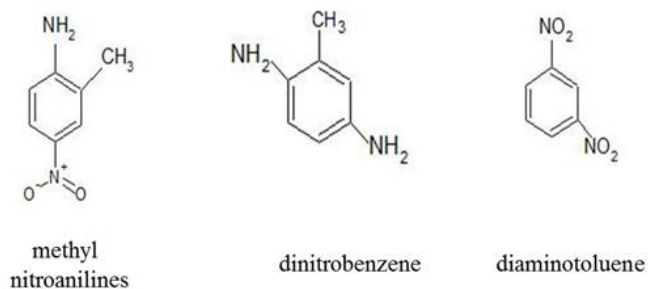
According to Chen & Liang (2008) and Dillert et al. (1995), photocatalytic degradation of 2,4-DNT in the presence of  $\text{TiO}_2$  begins with the cleaving of a nitro group by hydroxyl radicals, resulting in 3-Nitrotoluene (3-NT) (see Figure 7). According to Dillert et al. (1995), the decrease in nitro groups on the aromatic ring increases the reactivity of the aromatic compound leading to the easier cleavage of the second nitro group and forming toluene. Toluene would then be oxidized to benzaldehyde, which

would then result in benzoic acid and finally mineralized products of carbon dioxide, nitrate ion and water through decarboxylation of the carbons in the benzene ring (Chen & Liang, 2008; Dillert et al., 1995).



**Figure 7 - Proposed 2,4-DNT degradation pathway in the presence of TiO<sub>2</sub> (Chen & Liang, 2008)**

An alternative degradation pathway proposed by Wen et al. (2011) results in intermediate products of methyl nitroanilines, dinitrobenzene, and diaminotoluene before mineralization into carbon, nitrate ions and water (see Figure 8) (Wen et al., 2011).

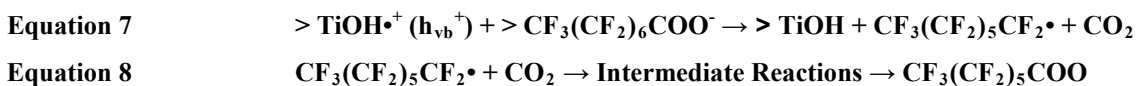


**Figure 8 - Alternate proposed intermediate products of 2, 4 -DNT degradation**

### **PFOA & PFOS Degradation Pathways in the Presence of TiO<sub>2</sub>**

According to Vecitis et al. (2009), TiO<sub>2</sub> photocatalytic degradation at environmentally relevant pH (pH = 6-8) proved very slow, but ultimately effective, for

decomposing PFOA. The degradation pathway involves the adsorption of PFOA onto the  $\text{TiO}_2$  which is then directly oxidized by a valence hole ( $h_{\text{vb}}^+$ ) produced by the excitation of the  $\text{TiO}_2$  electrons into the conduction band when the energy band gap is met or exceeded (Vecitis et al., 2009; Department of Health and Human Services, 2009). Equation 7 and Equation 8 indicate the cleaving of the carboxylic headgroup initially occurs followed by numerous intermediate reactions leading to the comparatively recalcitrant perfluoroheptanoate, a PFCA containing one less fluorinated carbon than PFOA in its chain. Subsequent reactions would continue similarly until the perfluorinated tail is completely unzipped (See Equations 7 & 8)(Vecitis et al., 2009; Department of Health and Human Services, 2009).



Vecitis et al. (2009) pointed out that  $\text{TiO}_2$  photocatalytic degradation at environmentally relevant pH was not effective in decomposing PFOS (Vecitis et al., 2009). This assessment is consistent with numerous investigations that used PFOS as an inert and reusable  $\text{TiO}_2$  surface coating to enhance the adsorption of hydrophobic contaminants (e.g. PCBs and chlorinated aromatics) onto the  $\text{TiO}_2$  surface to enhance its photocatalytic reactivity (Vecitis et al., 2009; Liu et al., 2004).

### **III. Methodology**

This chapter discusses the methodology used to investigate and answered the research questions posed for this research effort. The methodology identifies the materials, light sources and instruments used in the experiments. This section also describes slide fabrication methods and degradation experimental procedures.

#### **Chemicals**

High purity chemicals (> 99%, unless otherwise noted) were obtained and used as received from the supplier: Acetic acid (Sigma-Aldrich, St Louis, MO); Tween 80 (Sigma-Aldrich, St Louis, MO); Isopropyl alcohol (Sigma-Aldrich, St Louis, MO); Titanium (IV) Isopropoxide (Sigma-Aldrich, St Luis, MO); 2,4-Dinitrotoluene (Sigma-Aldrich, St Louis, MO); Silver nitrate (Wellington Labs, Merriam, KS); Perfluorooctanoic acid (Wellington Labs, Merriam, KS); (Na) Perfluorooctane sulfonate (Wellington Labs, Merriam, KS); Native Perfluorinated Acid/Sulfonate Mix (Wellington Labs, Merriam, KS).

#### **Light Sources and Analytical Instruments**

Experiments were conducted in natural sunlight and under UV light in Dayton, Ohio, coordinates 39.8 N, 84.2 W during the months of October-January. Natural sunlight experiments (conducted October-December) were placed outside in direct sunlight on clear days between 0900 and 1600. All Petri dishes were covered during the experiments to eliminate the effect of evaporation on the reactions. Temperature and solar irradiation levels were gathered and a statistical analysis of data was used to

evaluate their impact on degradation constants (see Chapter IV). UV light experiments (conducted under controlled laboratory conditions) were illuminated by a TripleBright II UV lamp (UV Systems, Inc., Renton, WA) at a distance of 2 cm from the reactors with a peak wavelength output of 254 nm and a 73.6 W power output. All aqueous solutions were prepared with ultra-pure deionized water (Millipore, 18.2 M  $\Omega\text{cm}$ ) prepared with a WaterPro PS Polishing Station (Labonco, Inc.).

A UV-Vis Spectrophotometry system (Agilent, Cary60) was used to measure 2,4-DNT concentration over time. The instrument has a 1.5 nm fixed spectral bandwidth and a wavelength range of 190-1100 nm. Wavelength accuracy is  $\pm 0.06$  at 250 nm and photometric accuracy is  $\pm 0.0007$ . A Gas Chromatography Mass Spectrometry system (GC-MS) (Agilent, GC 7890A) was also used to measure 2,4-DNT concentration over time and identify daughter products formed by the degradation reactions of 2,4-DNT.

In collaboration with the U.S. Environmental Protection Agency's National Risk Management Research Laboratory in Cincinnati, Ohio, a Liquid Chromatography-Mass Spectrometry system (LCMS) (ThermoFinnigan, LCQ Classic) and an EPA-developed analytical method were used to determine the concentration of PFOA and PFOS over time, along with the identification of products resulting from the photocatalytic reactions. A ZORBAX Eclipse XDB C-18 (Agilent Technologies) Rapid Resolution HT 600bar column with dimensions 4.6mm $\times$ 50mm, 1.8  $\mu\text{m}$  was used for the chromatographic separation of sample components. Column temperature was set at 50°C. The binary mobile phase was a solution of 10mM Formic acid (Solvent A) and 10mM Formic acid (Solvent B) in MeOH. See Table 5 for the gradient mobile phase program.

**Table 5 - Gradient mobile phase program**

Time (min)	Flow Rate ( $\mu\text{L min}^{-1}$ )	Solvent A %	Solvent B %
Initial	400	70	30
0.5	400	70	30
3	400	40	60
8	400	0	100
9	400	70	30
11	400	70	30

A Raman Spectroscopy system (LabRAM HR 800, Horiba Jobin Yvon, Inc.) with a 532.134 diode-pumped solid-state (DPSS) frequency-doubled Nd:YAG (Laser Quantum) excitation source and a spectral range of 100 - 4,000  $\text{cm}^{-1}$  was used to record and characterize the Raman spectra of the different areas of newly prepared  $\text{TiO}_2$  slides prior to use. A Scanning Electron Microscope (SEM) (Quanta 450, FEI, Inc.) was used to take images of pristine,  $\text{TiO}_2$ , and Ag- $\text{TiO}_2$  slides prior to use in order to characterize the film morphology at an accelerating voltage of 5kV.

#### **Fabrication of uncoated and silver-coated $\text{TiO}_2$ films on glass substrates**

Uncoated and silver-coated  $\text{TiO}_2$  thin films on glass substrates were fabricated using a modified sol-gel method in order to ensure high crystallinity of  $\text{TiO}_2$  (Han et al., 2011). Plain blank microscope slides (3 in X 1 in and 1 mm thick) were supplied by Fisher Scientific. To prepare uncoated  $\text{TiO}_2$  films on glass substrates, undoped  $\text{TiO}_2$  colloidal solution was prepared by combining 4.55 mL pure Tween 80 and 40.15 mL isopropanol in a 100 mL beaker. The solution was stirred using a magnetic stirrer at room temperature and after 5 minutes 0.67 mL acetic acid (17.4 M) and 3.4 mL of titanium (IV) Isopropoxide were added and stirred for an additional 20 minutes. Silver-



doped TiO<sub>2</sub> slides were prepared as above with the additional steps of adding appropriate amounts of AgNO<sub>3</sub> (99.9%) to the resulting solution (three concentrations of AgNO<sub>3</sub> were initially evaluated for effectiveness of 2,4-DNT degradation - see Chapter IV) and stirring for 12 hours to ensure homogenous dispersion of Ag<sup>+</sup> ions.

Before coating the pristine microscopic slides were rinsed with ethanol and dried in an oven at temperatures 80-100°C for 15 minutes. Undoped TiO<sub>2</sub> and Ag-TiO<sub>2</sub> films on glass substrates were manually dipped in their respective solutions for 18 seconds and dried in the open for 10 minutes. After the dip coating procedure, the slides were placed in a conventional oven for calcination. Slides were calcined at 500°C for 20 minutes and then cooled at room temperature for 10 minutes. All slides were dipped and calcined four additional times (i.e. a total of five treatment cycles).

## **Experimental Procedures**

Batch NAC experiments using 2,4-DNT were conducted under natural sunlight (outside) and UV light (in a laboratory environment) from October until January under atmospheric pressure. Batch PFC degradation experiments using PFOA and PFOS were conducted under UV light in a laboratory environment under atmospheric pressure.

Three conditions were tested: (1) target contaminants in the presence of slides coated with TiO<sub>2</sub> film, (2) target contaminants in the presence of slides coated with Ag-TiO<sub>2</sub> film and (3) target contaminants only as controls. Separate Pyrex glass-covered Petri dishes (Sigma-Aldrich, St Louis, MO) with 20 ml of 2,4-DNT (10 mg L<sup>-1</sup>), PFOA (0.1 mg L<sup>-1</sup>), and PFOS (0.1 mg L<sup>-1</sup>) solution in water were placed in direct sunlight on clear days between 0900 and 1700 and in UV light in a controlled environment. During all

experiments, Petri dishes without slides were used as controls. Every two hours a 1 mL sample was removed from each Petri dish and the concentration of the target contaminant was measured, along with an analysis to identify daughter products formed by the degradation of the target contaminants. Experiments were performed in duplicate and concentrations measured as a function of time.

### Degradation Kinetics

Results of past studies indicate first-order kinetics can be used to model the photocatalytic degradation of the target contaminants (Cao et al., 2010; Celin et al., 2003; Department of Health and Human Services, 2013; Herrmann, 1999; Wen et al., 2011; Zhao & Zhang, 2009). First-order kinetics indicates that target contaminants decrease exponentially over time (Equation 9) and their degradation rates are proportional to their concentration (Equation 10).

**Equation 9**

$$C = C_0 e^{-kt}$$

**Equation 10**

$$rate = \frac{dC}{dt} = -kC$$

**C - Model contaminant concentration at time t**

**C<sub>0</sub> - Initial model contaminant concentration at time 0**

**k - First-order rate constant (obtained by plotting ln(C/C<sub>0</sub>) vs. time data and calculating the slope of the line)**

**t - Time (min)**

An analysis of variance was performed to determine statistical differences between results. Results were also compared with previous studies that looked at the

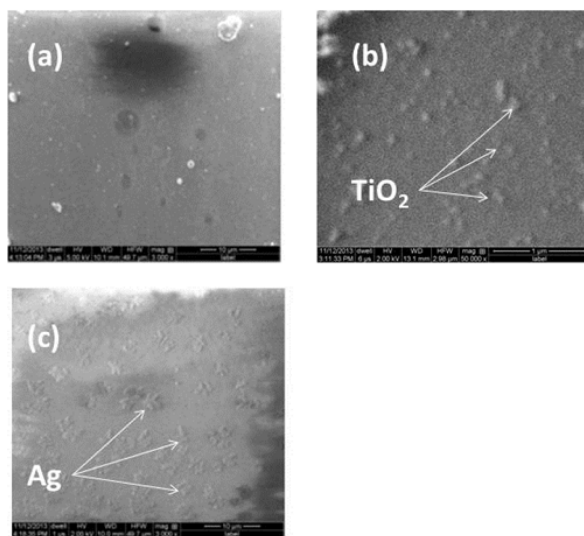
similar contaminants. Finally, an analysis and discussion of results is presented in in Chapter IV.

## **IV. Analysis and Results**

This chapter presents an analysis of the results from the batch experiments conducted for this research to assess the photocatalytic effectiveness of the treatments used to degrade 2,4-DNT, PFOA, and PFOS. Photocatalyst morphology, contaminant degradation rates and daughter product formation results are presented and analyzed.

### **TiO<sub>2</sub> and Ag-TiO<sub>2</sub> Slide Characterization**

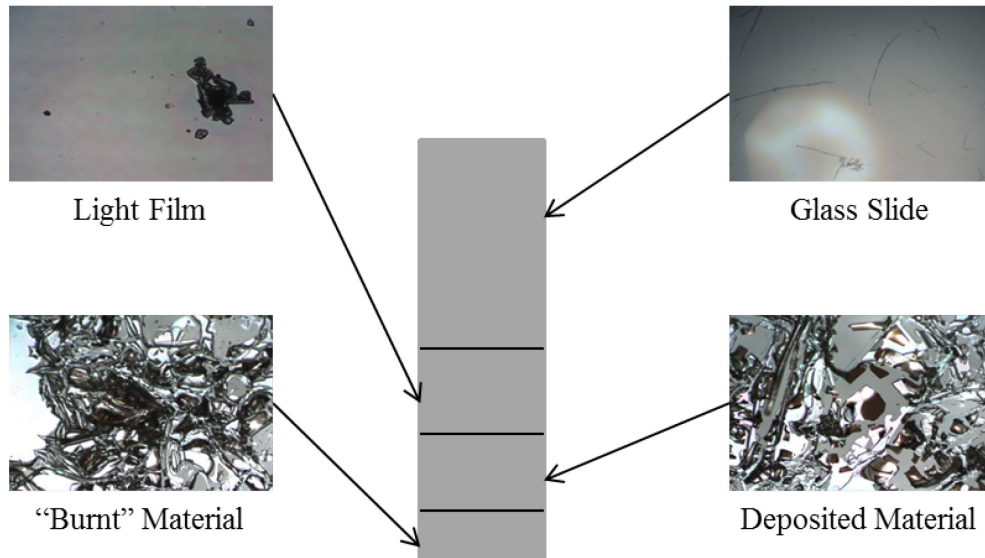
Undoped and silver-doped TiO<sub>2</sub> films on glass substrates were fabricated using a modified sol-gel method (Han et al., 2011). Scanning electron microscopy (SEM) was used to characterize the slides and the shape of the titanium dioxide and silver particles (Figure 9). Dispersed particles appeared on the glass surface when coated with TiO<sub>2</sub> nanoparticles (Figure 9b). Ag-TiO<sub>2</sub> appeared on the glass film as nanoparticle clusters (Figure 9c). Clustering appears in both TiO<sub>2</sub> and Ag-TiO<sub>2</sub> slides which may be responsible for lower than expected TiO<sub>2</sub> degradation rates of the target contaminants due to possibly reduced surface area.



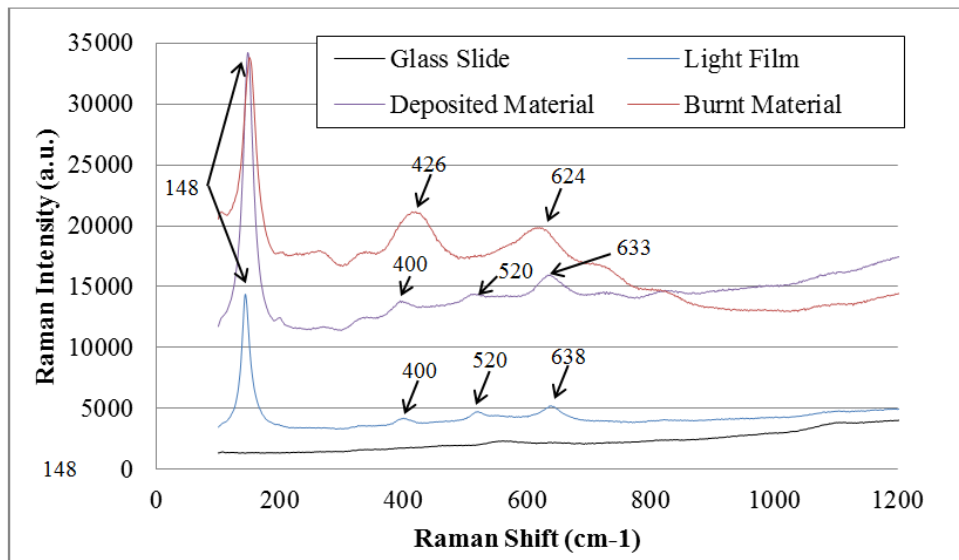
**Figure 9 - SEM micrographs showing (a) unmodified glass slides; (b) undoped TiO<sub>2</sub> film on glass slide; (c) Ag-TiO<sub>2</sub> film on glass slide**

Raman spectroscopy was used to characterize the TiO<sub>2</sub> slides. Figure 10 depicts optical images obtained prior to spectrum acquisition of the different areas of a pristine TiO<sub>2</sub> fabricated slide. Figure 11 displays the Raman spectra of the different areas of a TiO<sub>2</sub> fabricated slide. Aside from the Raman spectra of the glass slide, the film exhibits major peaks at 148 cm<sup>-1</sup>, 400 cm<sup>-1</sup>, 520 cm<sup>-1</sup>, and 638 cm<sup>-1</sup> which are very close to reference values of bulk anatase TiO<sub>2</sub> (Figure 12) found in the literature, confirming the presence of TiO<sub>2</sub> on the slides (Hardcastle, 2011). The optical images and Raman Spectra graph indicate the uneven coating of TiO<sub>2</sub> annealed to the glass slide, which is likely responsible for the decreased effectiveness in degrading target compounds. Imperfect slide fabrication can be attributed to the slide fabrication methodology used in this study compared to other studies that used a mechanical dip-coating machine to maintain a constant withdrawal velocity, thereby resulting in an even coating, and a

programmable oven which allows for a more controlled annealing process (Han et al., 2011).



**Figure 10 - Optical images of  $\text{TiO}_2$  slide obtained prior to spectrum acquisition. Total slide dimensions: 7.6 cm x 2.5 cm. Uncoated dimensions (one side): 4.6 cm x 2.5 cm. Coating dimensions (one side): 3.0 cm x 2.5 cm**



**Figure 11 - Raman spectra of the  $\text{TiO}_2$  on fabricated slides**

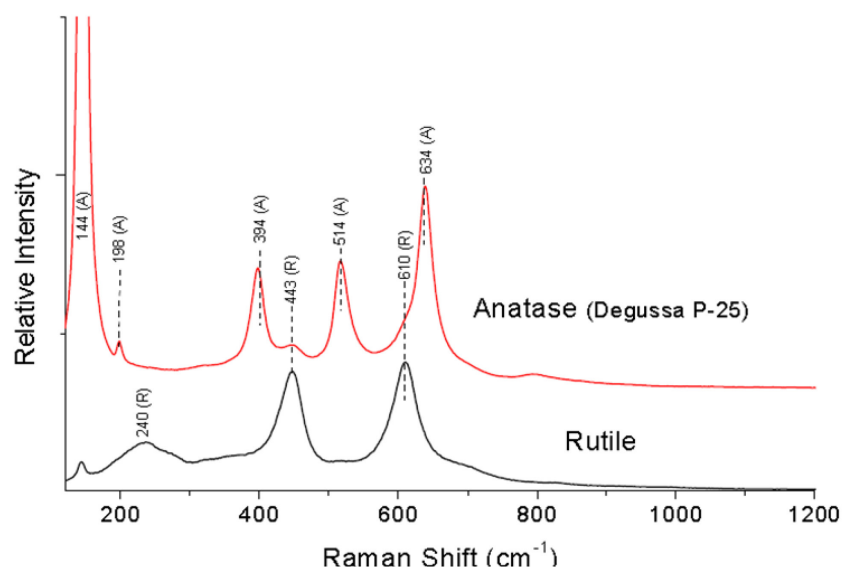


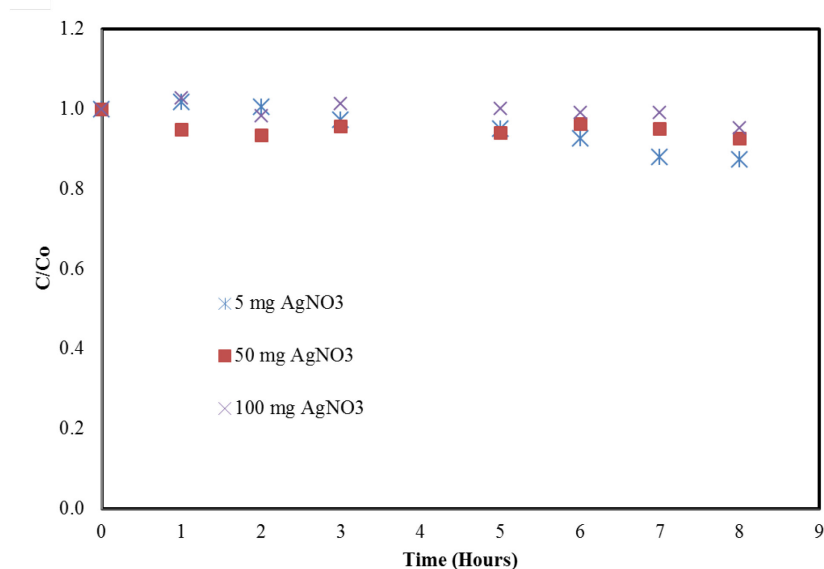
Figure 12 - Reference Raman spectra of  $\text{TiO}_2$  bulk reference compounds: anatase and Rutile (Hardcastle, 2011)

### *Effects of $\text{AgNO}_3$ concentration on $\text{Ag-TiO}_2$ slides*

A review of the literature indicates that there is an optimal  $\text{Ag}^+$  concentration that will maximize the efficiency of the  $\text{Ag-TiO}_2$  slides. Daghrir et al. (2013) asserts that an optimum mole fraction of  $\text{Ag}^+$  doping (2-4 mol % moles Ag per mole  $\text{TiO}_2$ ) could effectively increase the photocatalytic activity of  $\text{TiO}_2$  by increasing the surface area of the catalyst while a further increase in  $\text{Ag}^+$  concentration could increase recombination of electrons/holes and thus lower its photocatalytic activity (Daghrir et al., 2013; Sobana et al., 2006). Sobana et al. (2006) indicated that silver doping of  $\text{TiO}_2$  increases its absorption in visible light as the content of Ag increases to an optimal level and reported that 1.5 wt. % Ag content was the optimal amount to achieve the most effective rate of Direct diazo dye red 23 photodegradation and 2.0 wt. % for Direct blue 53 (Sobana et al., 2006). Arabatzis et al. (2003) reported maximum photocatalytic degradation of methyl

orange when exposed to dispersed TiO<sub>2</sub> modified in 10<sup>-3</sup> M AgNO<sub>3</sub> solution (Arabatzis et al., 2003).

In this study three different concentrations of AgNO<sub>3</sub> were tested during Ag-TiO<sub>2</sub> slide fabrication. UV-Vis analysis results of 2,4-DNT degradation in sunlight using Ag-TiO<sub>2</sub> slides dipped in solutions containing 5 mg (0.005% mol), 50 mg (0.05% mol) and 100 mg (0.107% mol) of AgNO<sub>3</sub> are shown in Figure 13. The results indicated no difference between AgNO<sub>3</sub> concentrations at the 95% confidence level. Thus, Ag-TiO<sub>2</sub> slides fabricated with 5 mg AgNO<sub>3</sub> were used throughout this study.



**Figure 13 - UV-Vis degradation results of 2,4-DNT by Ag-TiO<sub>2</sub> films on glass substrate using different concentrations of AgNO<sub>3</sub> during slide fabrication. Experimental conditions: degradation of 2,4-DNT (10 mg L<sup>-1</sup>) under sunlight in the presence of Ag-TiO<sub>2</sub> slides. The area of the films was 15 sq. cm in each test.**



## **Degradation Kinetics**

As found in earlier studies (Mihas et al., 2007; Wen et al., 2011; Dillert et al., 1995), the degradation data of 2,4-DNT corresponds well to a first-order kinetic model. Degradation results for PFOA and PFOS, discussed below, do not indicate that decomposition occurred and, as such, modeling of their degradation kinetics was not possible.

## **Experimental Results**

Photocatalytic degradation experiments using 2,4-DNT, PFOA, and PFOS were performed to study the effect different treatments had on the contaminants' concentration over time and daughter product formation. All 2,4-DNT experiments were conducted in an aqueous solution at a concentration of  $10 \text{ mg L}^{-1}$  and all PFOA and PFOS experiments were conducted at a concentration of  $0.1 \text{ mg L}^{-1}$ . External factors (i.e., pH levels, temperature, irradiation intensities, and solution volumes) for all batch experiments under UV light were controlled. For batch experiments in sunlight certain external factors (i.e., pH levels and solution volumes) were controlled. Although the experiments under sunlight were conducted outdoors under similar clear and sunny conditions, some factors (i.e., solar irradiation intensities and temperature), which couldn't be controlled, were statistically analyzed to determine their effect, if any, on experimental results. See Table 6 for summary of results.

**Table 6 - Summary of photocatalytic UV-Vis and GCMS results by treatment for 2,4-DNT**

<i>Treatment</i>	<i>Measured by UV-Vis 1st Order degradation rate (hr<sup>-1</sup>)</i>	<i>Measured by GCMS</i>
AgTiO <sub>2</sub> (in UV)	0.020	-
AgTiO <sub>2</sub> (in Solar)	0.022	-
TiO <sub>2</sub> (in UV)	0.045	0.051
TiO <sub>2</sub> (in Solar)	0.030	-
Control (in UV)	0.003	0.012
Control (in Solar)	0.007	-

### ***Effects of Temperature and Solar Irradiation on Photocatalytic Reactions***

To determine the effects of temperature on experiments conducted outside, the mean air temperature was collected during all experiments. An analysis of variance between the degradation rates over time of similar experiments was done to determine the effect of temperature variations on the photocatalytic reactions. The statistical analysis indicated the degradation rates between batches did not differ at the 95% confidence level.

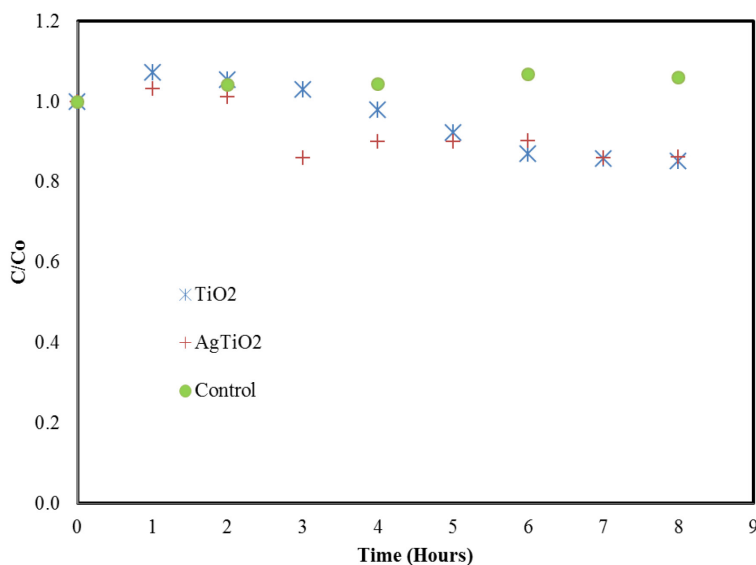
To determine the effects of varying solar irradiation levels, historical weather data were gathered and analyzed in conjunction with the experimental results to determine the effect of solar irradiation on the photocatalytic reaction rates. Historical solar radiation data for Wright Patterson Air Force Base, Ohio from October - December were obtained from the National Renewable Energy Laboratory (Department of Energy, 2012). The data shows extraterrestrial radiation (ETR), a point on top of the Earth's atmosphere

normal to the Sun's rays, only fluctuating between 1,369 - 1,431 W-h m<sup>-2</sup> during the days outdoor experiments were conducted (Paulescu et al., 2013). As all the outdoor experiments were conducted under similar cloudless weather conditions, we can assume that the variability in solar radiation for these experiments was minimal. Ultimately, an analysis of variance between similar experiments conducted in natural sunlight did not differ at the 95% confidence level.

### ***Degradation of 2,4-DNT***

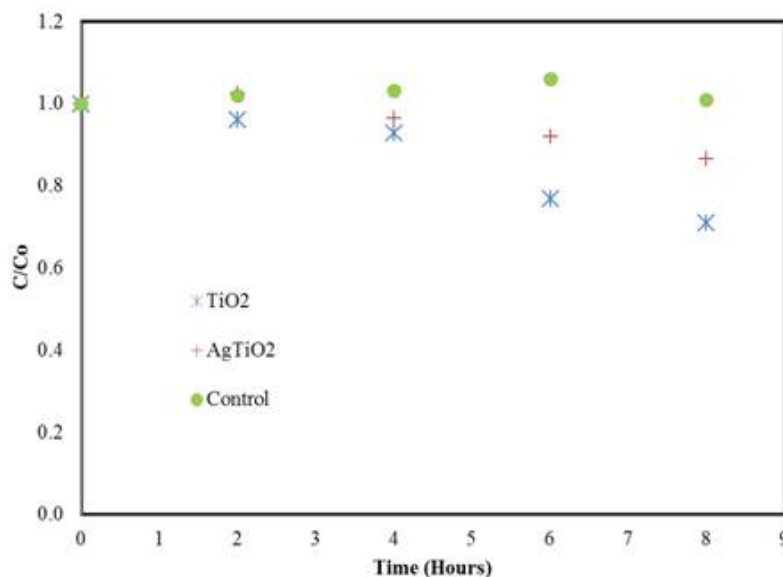
UV-Vis analysis results indicate that the removal of 2,4-DNT under solar radiation in the presence of Ag-TiO<sub>2</sub> slides was found to be 14% after 8 hours (Figure 14) and compared to the control (i.e., sunlight only) the results were significant at the 95% confidence level. UV-Vis analysis results indicate that the removal of 2,4-DNT under solar radiation in the presence of TiO<sub>2</sub> slides was found to be 15% after 8 hours (Figure 14) and compared to the control the results were significant at the 95% confidence level. However, a statistical analysis of the degradation results of TiO<sub>2</sub> and Ag-TiO<sub>2</sub> treatments under solar light shows that the treatments do not differ at the 95% confidence level. These results indicate that doping TiO<sub>2</sub> with Ag did not enhance the catalyst's performance under sunlight, signifying that undoped TiO<sub>2</sub> is just as effective without the addition of silver. Additionally, the degradation rates observed are considerably lower than expected. The degradation constant achieved of 0.022 h<sup>-1</sup> (2,4-DNT - 10 mg L<sup>-1</sup>) in the presence of Ag-TiO<sub>2</sub> under sunlight was lower than the rate

constant of  $0.132 \text{ h}^{-1}$  achieved by Mihas et al (2007) in degrading 2,4-DNT ( $1 \text{ mg L}^{-1}$ ) under sunlight only (Mihas et al., 2007).



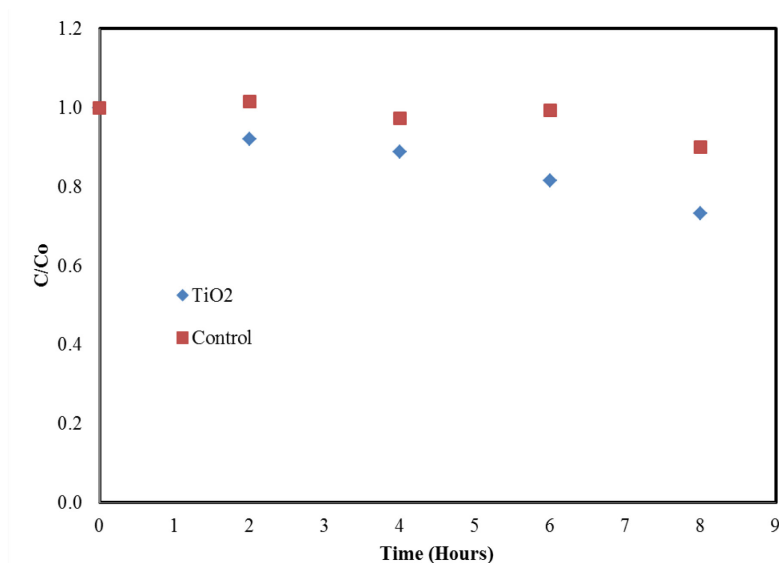
**Figure 14 - UV-Vis measured degradation results of 2,4-DNT by TiO<sub>2</sub> and Ag-TiO<sub>2</sub> films on glass substrates under sunlight. Experimental conditions: degradation of 2,4-DNT ( $10 \text{ mg L}^{-1}$ ) under sunlight in the presence of TiO<sub>2</sub> and Ag-TiO<sub>2</sub> slides. 5 mg of AgNO<sub>3</sub> used to fabricate Ag-TiO<sub>2</sub> slides. The area of the films used was 15 sq. cm in each test.**

UV-Vis analysis results indicate that the removal of 2,4-DNT under UV light in the presence of Ag-TiO<sub>2</sub> slides was found to be 13% after 8 hours (Figure 15). However, compared to the control, the results were not significantly different at the 95% confidence level. A comparison of these results with results obtained from Ag-TiO<sub>2</sub> under solar light shows that there is no difference in degradation rate at the 95% confidence level. These results indicate that doping TiO<sub>2</sub> with Ag did not enhance the photocatalytic effectiveness of TiO<sub>2</sub> suggesting that the Ag<sup>+</sup> concentration used was not effective as an electron trap under UV light as would be expected (Sobana et al., 2006).

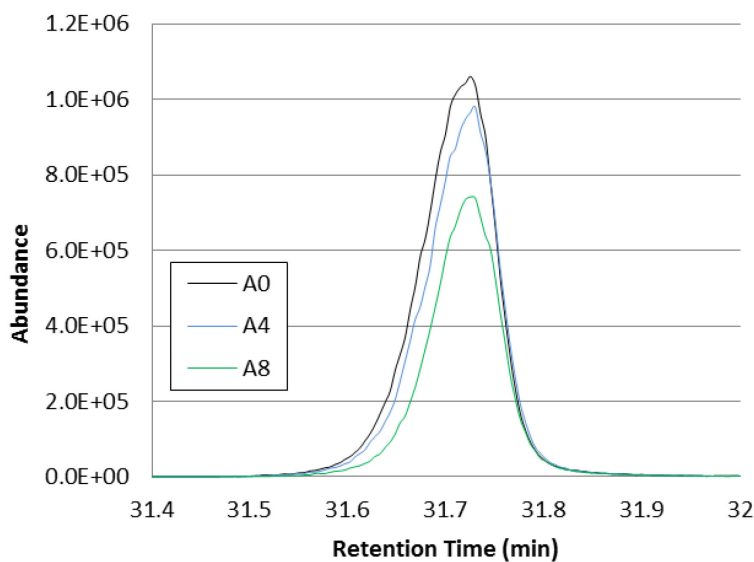


**Figure 15 - UV-Vis measured degradation results of 2,4-DNT by TiO<sub>2</sub> and Ag-TiO<sub>2</sub> films on glass substrates under UV light. Experimental conditions: degradation of 2,4-DNT (10 mg L<sup>-1</sup>) under UV light in the presence of TiO<sub>2</sub> and Ag-TiO<sub>2</sub> slides. The area of the films used was 15 sq. cm in each test.**

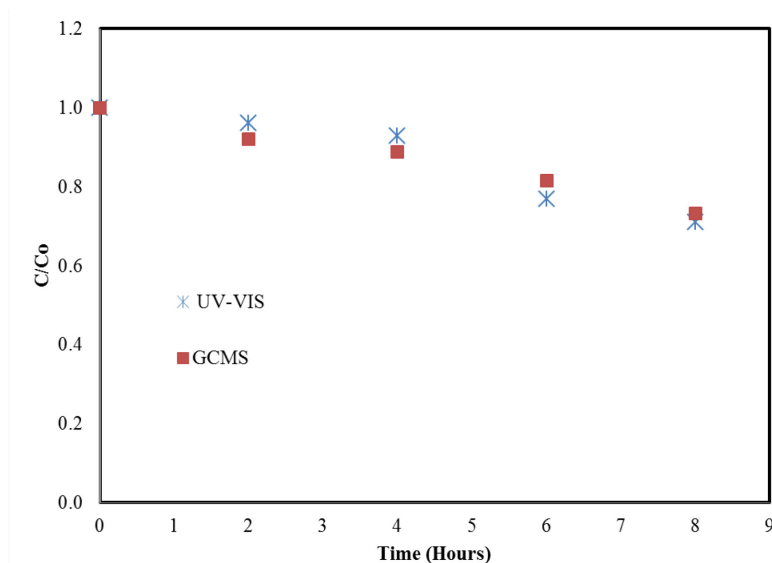
Finally, UV-Vis analysis results indicate that the removal of 2,4-DNT under UV radiation in the presence of TiO<sub>2</sub> slides was found to be 29% after 8 hours (Figure 15) and compared to the control (i.e., UV radiation only) the results differ at the 95% confidence level. 2,4-DNT degradation rates under UV light in the presence of TiO<sub>2</sub> slides were also measured with a GCMS analysis. GCMS results indicated that 2,4-DNT decomposed 30% after 8 hours (Figure 16 and Figure 17) and compared to the control the results differ at the 95% confidence level. The results of the UV-Vis and GCMS analyses (Figure 18) are similar at the 95% confidence level indicating the accuracy of previous results from UV-Vis analysis. The degradation rate constant ( $k = 0.045 \text{ h}^{-1}$ ) achieved for degrading 2,4-DNT (10 mg L<sup>-1</sup>) in the presence of TiO<sub>2</sub> and under UV light is lower than the degradation rate constant ( $k = 0.24 \text{ h}^{-1}$ ) achieved by Wen et al. (2011) in degrading 2,4-DNT (50 mg L<sup>-1</sup>) in the presence of immobilized TiO<sub>2</sub> under UV light.



**Figure 16 - GCMS measured degradation results of 2,4-DNT by TiO<sub>2</sub> films on glass substrates. Experimental conditions: degradation of 2,4-DNT (10 mg L<sup>-1</sup>) under UV light with TiO<sub>2</sub>. The area of the films used was 15 sq. cm. in each test.**



**Figure 17 - GCMS results for 2,4-DNT degradation at time 0 hr. [(A0) to 8 hr. (A8)]. Experimental conditions: degradation of 2,4-DNT (10 mg L<sup>-1</sup>) under UV light with pristine TiO<sub>2</sub>. The area of the films used was 15 sq. cm. in each test**

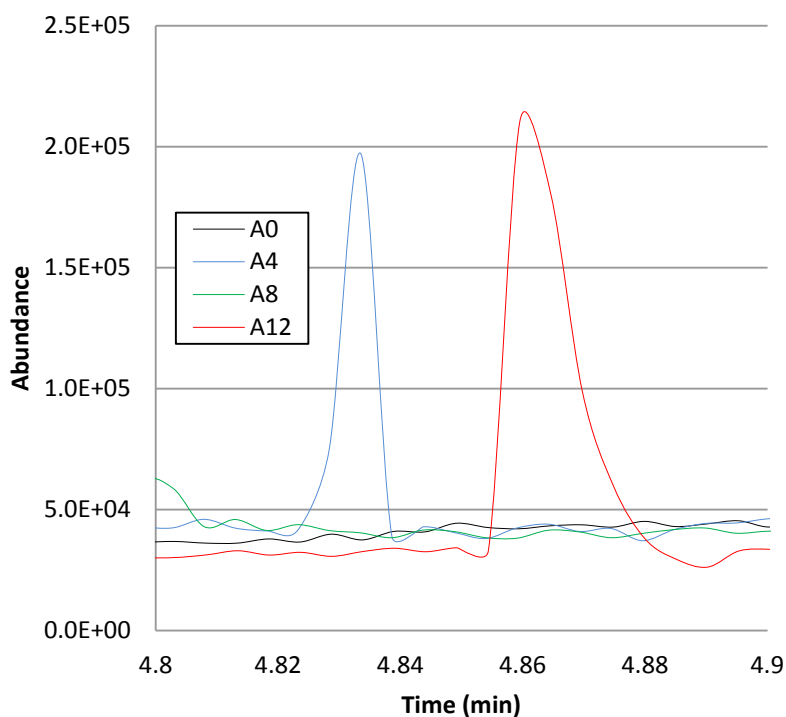


**Figure 18 - GCMS and UV-Vis measured degradation results of 2,4-DNT by TiO<sub>2</sub> films on glass substrates. Experimental conditions: degradation of 2,4-DNT (10 mg L<sup>-1</sup>) under UV light with pristine TiO<sub>2</sub>. The area of the films used was 15 sq. cm. in each test.**

### ***Unknown Byproducts of 2,4-DNT Degradation***

The 2,4-DNT batch experiments that were conducted using TiO<sub>2</sub> slides under UV light for 12 hours were analyzed by GCMS to identify degradation byproducts. The data clearly indicated the degradation of 2,4-DNT over time (Figure 16 & Figure 17); however the expected byproducts of amino nitrotoluenes (methyl nitroanilines), dinitrobenzene, diaminotoluene, *o*-mononitrotoluene, toluene, benzaldehyde, and benzoic acid could not be identified (Chen & Liang, 2008; Dillert et al., 2007; Wen et al., 2011). GCMS retention time (RT) data indicated unknown compounds between the RT = 2 minutes and RT = 5 minutes that apparently are not associated or correlated with 2,4-DNT degradation. However an unknown byproduct was seen at RT = 4.8 minutes that correlated with the degradation of 2,4-DNT. Figure 19 shows the abundance profile of

this unknown byproduct over time [0 hour (A0) to 12 hour (A12)], showing zero abundance at time 0 which corresponds to an initial concentration of 2,4-DNT ( $C/C_0 = 1.00$ ). At time 4 hours the abundance increases and then at 8 hours returns to its original abundance followed by an increase at time 12 hour. This abundance profile over time indicates that the unknown compound is possibly a byproduct of 2,4-DNT degradation; however since 2,4-DNT is degrading at a constant rate it appears to be complex interactions with the photocatalytic reactions and the other unknown compounds. Consequently, the correlation between the 2,4-DNT degradation and this unknown compound is inconclusive.

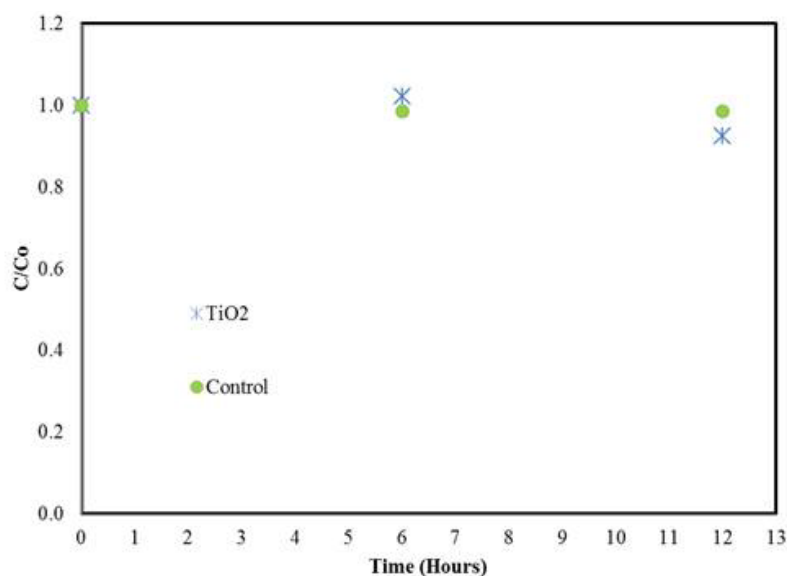


**Figure 19 - GCMS results for unknown byproduct at time 0 hr. (A0) to 12 hr. (A12). Experimental conditions: degradation of 2,4-DNT ( $10 \text{ mg L}^{-1}$ ) under UV light with pristine  $\text{TiO}_2$ . The area of the films used was 15 sq. cm. in each test.**

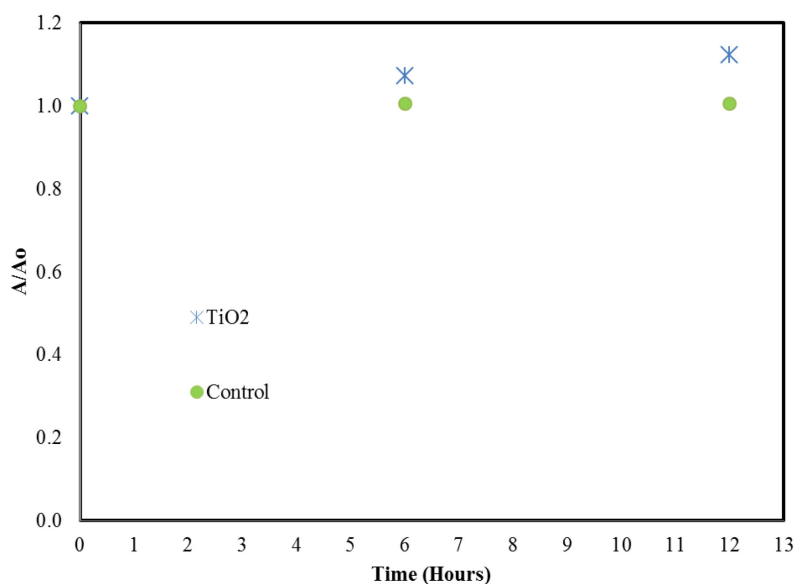


### ***Degradation of PFOA and PFOS***

LCMS analysis results of PFOA degradation experiments in the presence of  $\text{TiO}_2$  slides under UV light did not indicate any degradation of PFOA after 12 hours (Figure 20). LCMS analysis results of PFOS degradation experiments in the presence of  $\text{TiO}_2$  slides under UV light could not be fully evaluated due to an inaccurate standard calibration curve identified during data analysis. As such the area ratio ( $A/A_0$ ) rather than concentration ratio ( $C/C_0$ ) was used to assess the nominal degradation of PFOS. The results shown in Figure 21 do not indicate degradation of PFOS after 12 hours.



**Figure 20 - LCMS degradation results of PFOA. Experimental conditions: degradation of PFOA ( $0.1 \text{ mg L}^{-1}$ ) under UV light in the presence of  $\text{TiO}_2$  slides. The area of the films used was  $15 \text{ sq. cm}$  in each test.**



**Figure 21 - LCMS degradation results of PFOS. Experimental conditions: degradation of PFOA (0.1 mg L<sup>-1</sup>) under UV light in the presence of TiO<sub>2</sub> slides. The area of the films used was 15 sq. cm in each test.**

The results of PFOA and PFOS degradation experiments under environmentally relevant pH conditions are consistent with the majority of the literature discussed previously. It is most likely that the resistance of PFOA and PFOS to photocatalytic oxidation by TiO<sub>2</sub> is attributed to a number of factors previously discussed: (1) relatively low energy potential of hydroxyl ions ( $E^0 - 1.9V$ ) to cleave the ionic headgroup ( $SO_3^-$ ,  $CO_2^-$ ) or break the C-F bonds; (2) the relatively low energy UV domain (254 nm) used for the experiments; and (3) the decreased efficiency of immobilized TiO<sub>2</sub> compared to dispersed TiO<sub>2</sub>. Additionally, the manual method of TiO<sub>2</sub> fabrication employed in this study may have played a role in reducing the treatment effectiveness.

## V. Conclusions and Recommendations

### Summary

This thesis explored different photocatalysts immobilized on glass slides and different types of irradiation with the goal of finding a simple, effective and energy efficient treatment using sunlight. In this study, the use of  $\text{TiO}_2$  and  $\text{Ag-TiO}_2$  as photocatalysts for the destruction of NACs and PFCs was investigated.  $\text{TiO}_2$  and  $\text{Ag-TiO}_2$  thin films were immobilized on microscope glass slides by the sol-gel method. Slides were characterized. Batch-scale experiments were then conducted to determine photocatalytic degradation rates of 2,4-DNT, PFOS and PFOA under different treatments, identify and characterize degradation daughter products, and model degradation kinetics. Degradation of 2,4-DNT in aqueous solution ( $10 \text{ mg L}^{-1}$ ) in the presence of  $\text{TiO}_2$  and  $\text{Ag-TiO}_2$  under sunlight and UV light was evaluated. Degradation of PFOA and PFOS in aqueous solution ( $0.1 \text{ mg L}^{-1}$ ) in the presence of  $\text{TiO}_2$  slides under UV light was also evaluated. Results were modeled using first-order kinetics to obtain degradation rate constants.

### Conclusions

**What are the photocatalytic degradation rates for PFOS, PFOA and 2,4-DNT using undoped  $\text{TiO}_2$  as a catalyst, compared to using  $\text{Ag-TiO}_2$  as a catalyst? -**

Experimental results (see Table 6) showed greater degradation of 2,4-DNT in the presence of  $\text{Ag-TiO}_2$  under sunlight compared to degradation by sunlight only. However compared with degradation by undoped- $\text{TiO}_2$  there was no statistical difference,

indicating that doping with silver is not an effective method to improve performance of the catalyst under the conditions of this study ( $10 \text{ mg L}^{-1}$  2,4-DNT in sunlight).

Experimental results showed the degradation of 2,4-DNT for  $\text{TiO}_2$  and  $\text{Ag-TiO}_2$  under UV light to be statistically different than UV light only. These results also indicated that 2,4-DNT degraded more than twice as fast in the presence of  $\text{TiO}_2$  than  $\text{Ag-TiO}_2$ , which is contrary to what is expected based on the literature. Finally, a comparison of the degradation of 2,4-DNT in the presence of  $\text{TiO}_2$  under UV light to previous similar studies indicate that the degradation rate are lower than would be expected.

Experimental results showed no degradation of PFOA and PFOS in the presence of  $\text{TiO}_2$  under UV light. These results, considered in combination with the 2,4-DNT results which showed Ag-doping did not improve 2,4-DNT degradation, suggest that treatment in the presence of  $\text{Ag-TiO}_2$  under solar light and UV light will also not degrade PFOA and PFOS. This conclusion is due to silver's apparent ineffectiveness in extending the sensitivity of  $\text{TiO}_2$  into the visual spectrum under sunlight.

**What is the difference between using UV light and natural solar light as energy sources for the photocatalytic treatment of PFOA, PFOS, and 2,4-DNT-contaminated water?** - Experimental results (see Table 6) show that in the presence of  $\text{TiO}_2$  2,4-DNT degrades faster under UV light compared to sunlight. These results are expected as the literature indicates that  $\text{TiO}_2$  requires light waves in the UVA domain (387 nm) to meet or exceed its band energy gap. Experimental results show that in the presence of  $\text{Ag-TiO}_2$  2,4-DNT degrades at the same rate under UV light and sunlight.

These results are expected as the literature indicates that under UV light Ag partially enhances  $\text{TiO}_2$ 's photocatalyst efficiency by only acting as an electron trap and under sunlight Ag acts as both an electron trap and photosensitizes  $\text{TiO}_2$ , so it can be suggested that both treatments produce comparable photocatalytic reaction rates. Overall, however, these results are lower than expected when compared to the degradation rate of 2,4-DNT in the presence of  $\text{TiO}_2$  under UV light.

**What are the daughter products of PFOS, PFOA, and 2,4-DNT photodegradation? -**

2,4-DNT degradation products could not be identified. GCMS data indicate an unknown byproduct that may be associated with the degradation of 2,4-DNT, however this could not be verified. Since LCMS data indicated no degradation of PFOA or PFOS, daughter product characterization was not possible.

**How does the composition of PFC and NAC degradation daughter products change over time during photodegradation? -** Since results were inconclusive in identifying 2,4-DNT degradation daughter products, it was not possible to characterize daughter product change over time was not possible. Since LCMS data indicated no degradation of PFOA or PFOS, daughter product characterization was not possible.

**How may the kinetics of PFOS, PFOA, and 2,4-DNT degradation be modeled? -**

Experimental results for 2,4-DNT indicate that first-order kinetics can be used to model 2,4-DNT degradation. LCMS data indicated no degradation of PFOA or PFOS.

## **Future Work**

**Improve slide fabrication.** The slide fabrication method relied on manual procedures.

A future study that uses more advanced fabrication methods would hopefully improve catalyst performance by ensuring homogenous film coatings on the entire glass substrate area. Also, better control of the annealing temperatures would serve to increase catalysts effectiveness.

**Optimize silver content.** Investigate the optimum silver content to degrade the target contaminants. Prior studies have shown that silver optimization should enhance the catalyst's effectiveness by ensuring maximum electron charge separation for generated electrons/holes on the  $\text{TiO}_2$  surface.

**Explore concentrated sunlight.** This study was conducted under direct sunlight. Exploring the use of mirrors to concentrate sunlight, thereby increasing the radiation energy, may enhance the effectiveness of the photocatalyst.

**Identify and characterize byproducts.** Photocatalysis of 2,4-DNT by  $\text{TiO}_2$  yielded some degradation; however the GCMS analysis could not identify daughter products. Employing an HPLC may allow for the identification of these byproducts and may lead to greater understanding of 2,4-DNT photocatalytic degradation.

**Extend studies to smaller-chain PFCs.** This study examined PFOA and PFOS, two long-chained PFCs, known to be recalcitrant to photocatalytic degradation. Success in degrading smaller-chained PFCs may lead to an effective treatment train strategy (i.e., treating PFOA and PFOS with one treatment method and treating the resulting daughter products with photocatalysis).

**Conduct cost analysis.** Conduct a cost analysis of this treatment compared to other treatments to assess its commercial potential. The simplicity and normal conditions (atmospheric conditions, neutral pH, ambient temperature ranges) associated with this treatment make it a promising and economic viable alternative to treat numerous contaminants.

## **Appendix A - Experimental Results**



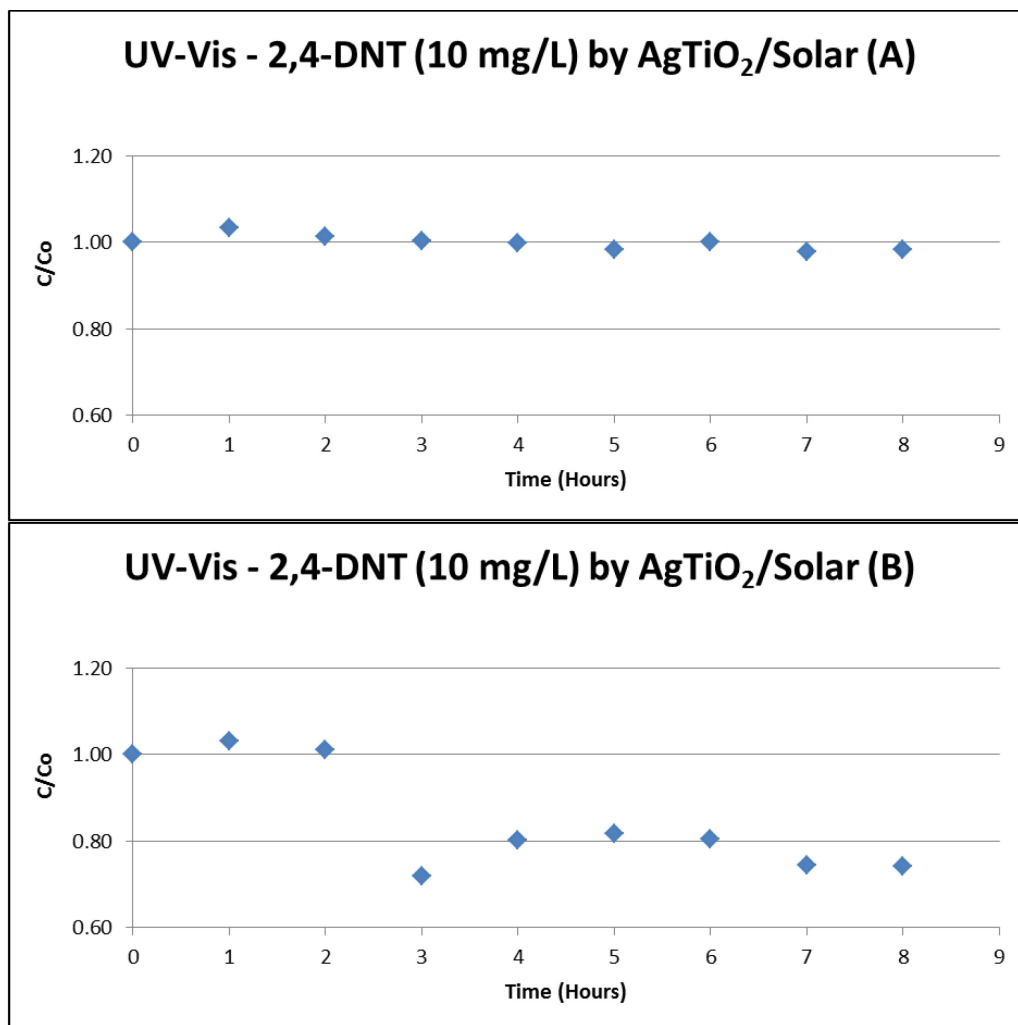


Figure 22 - UV-Vis experiment results (A) and (B) - 2,4-DNT (10 mg L<sup>-1</sup>), Ag-TiO<sub>2</sub>/solar light

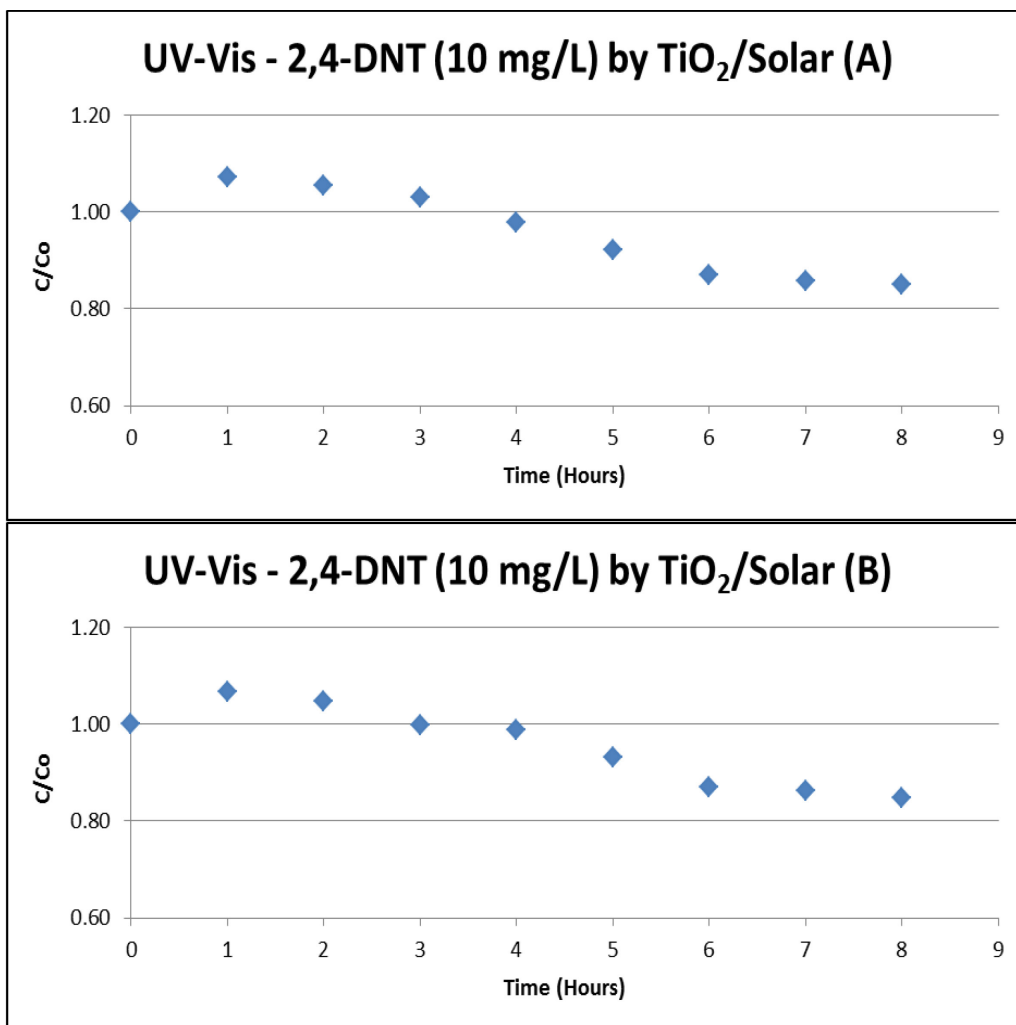


Figure 23 - UV-Vis experiment results (A) and (B) - 2,4-DNT (10 mg L<sup>-1</sup>), TiO<sub>2</sub>/solar light

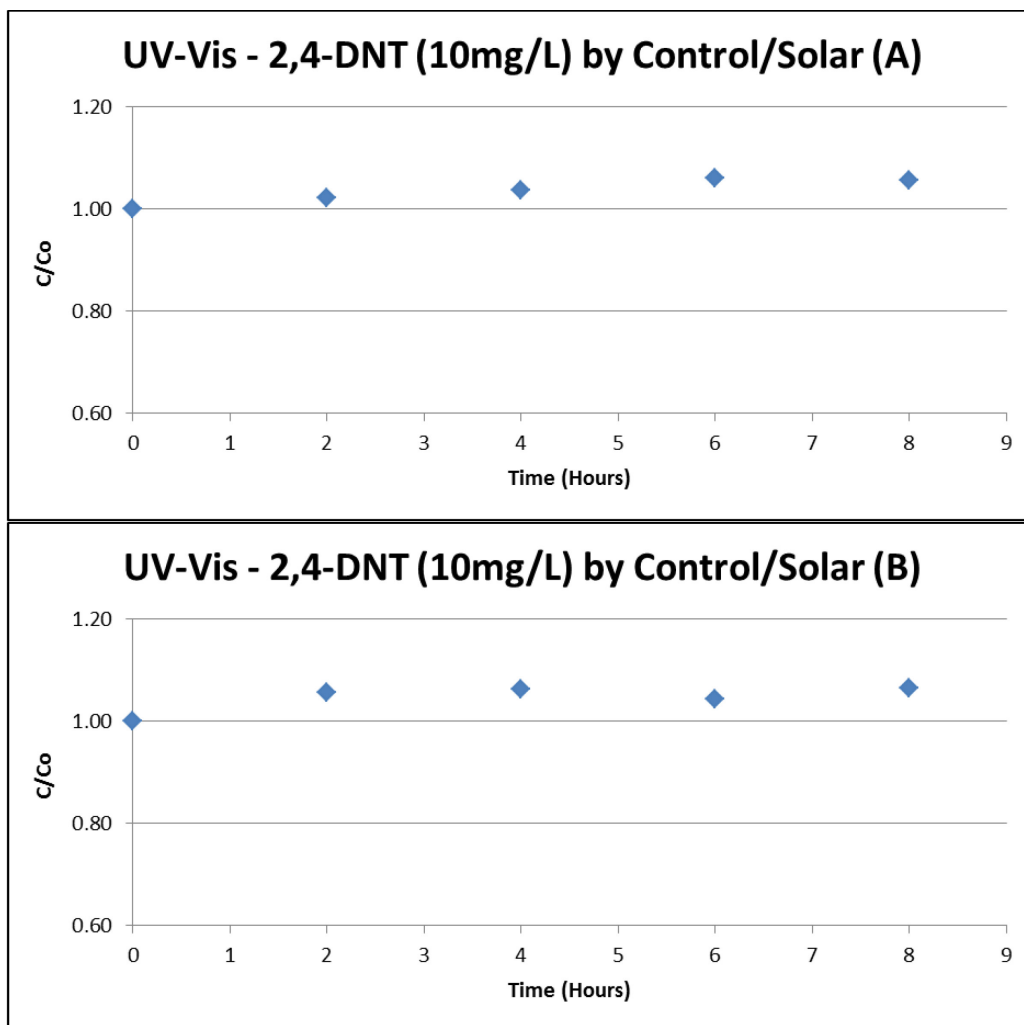


Figure 24 - UV-Vis experiment results (A) and (B) - 2,4-DNT (10 mg L<sup>-1</sup>), Control/solar light

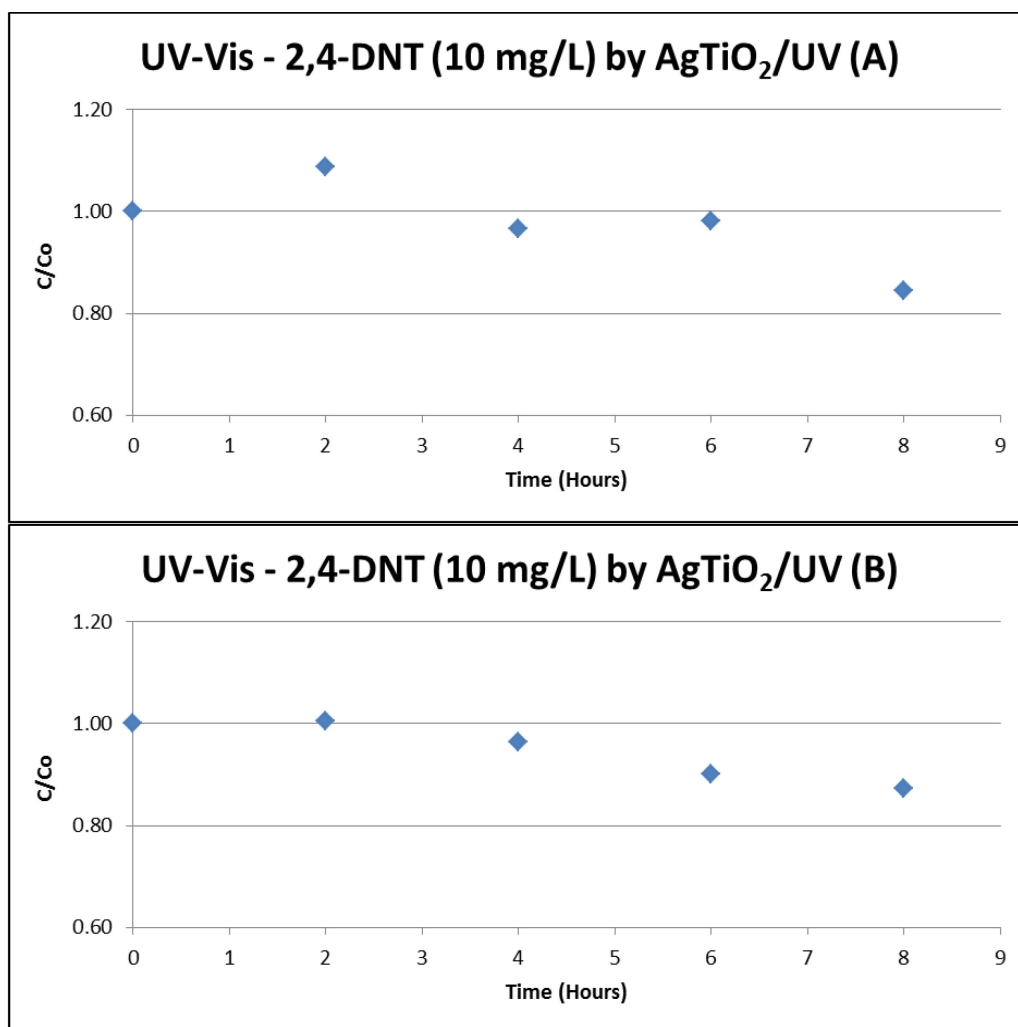


Figure 25 - UV-Vis experiment results (A) and (B) - 2,4-DNT (10 mg L<sup>-1</sup>), Ag-TiO<sub>2</sub>/UV light

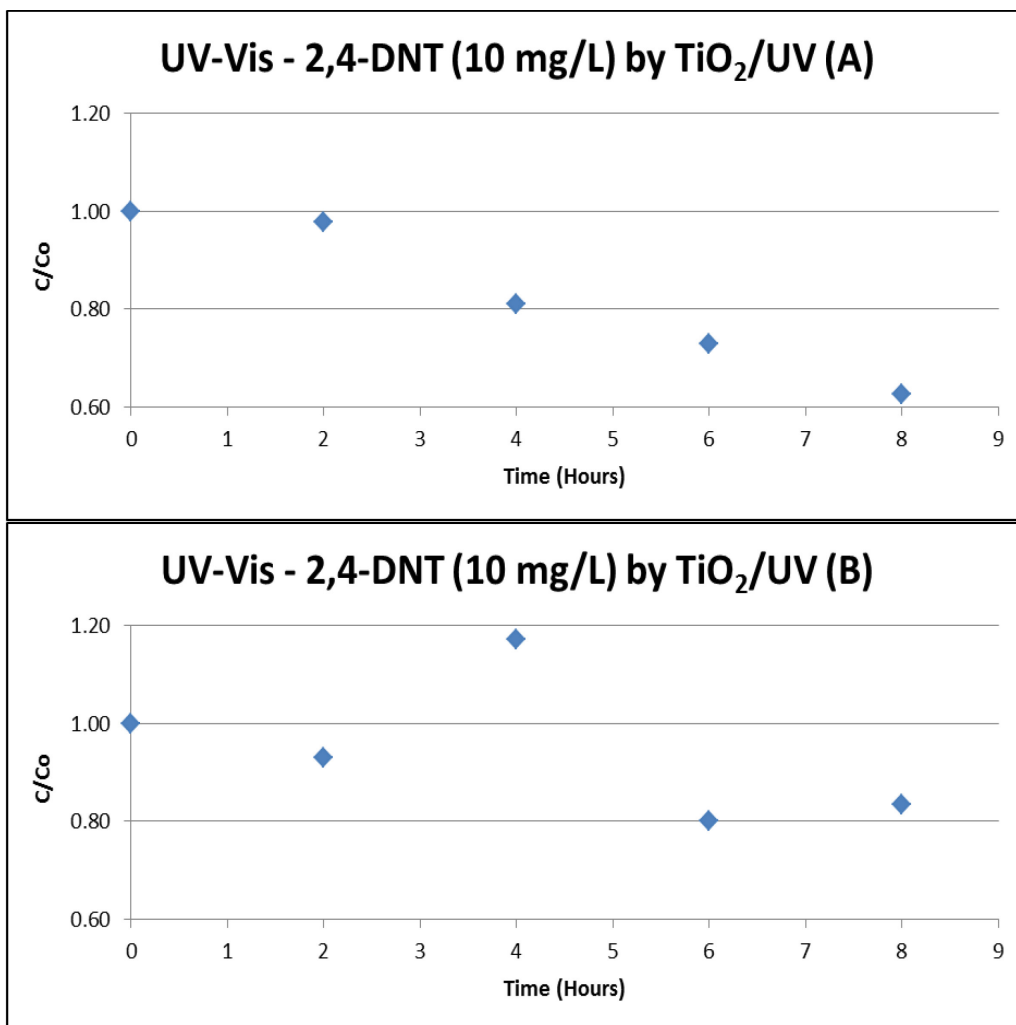


Figure 26 - UV-Vis experiment results (A) and (B) - 2,4-DNT ( $10 \text{ mg L}^{-1}$ ),  $TiO_2$ /UV light

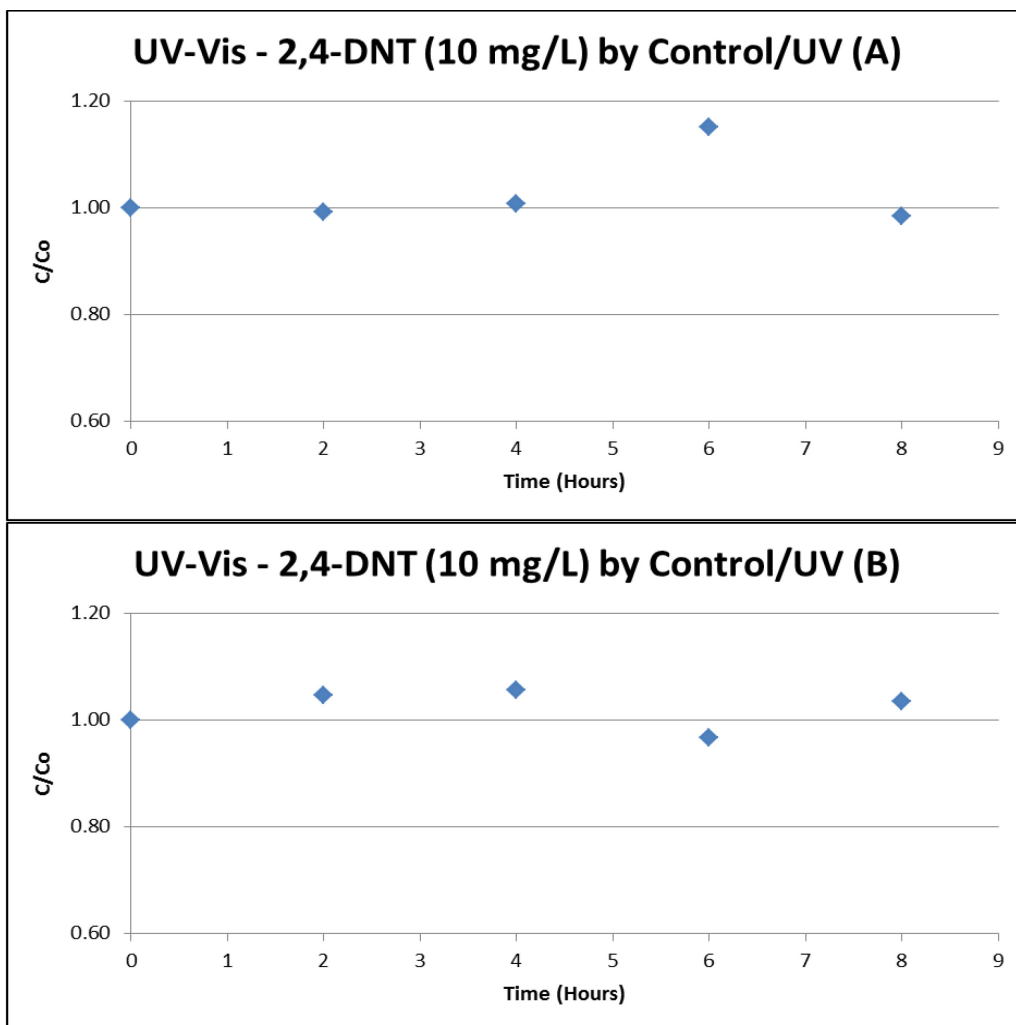


Figure 27 - UV-Vis experiment results (A) and (B) - 2,4-DNT (10 mg L<sup>-1</sup>), Control/UV light

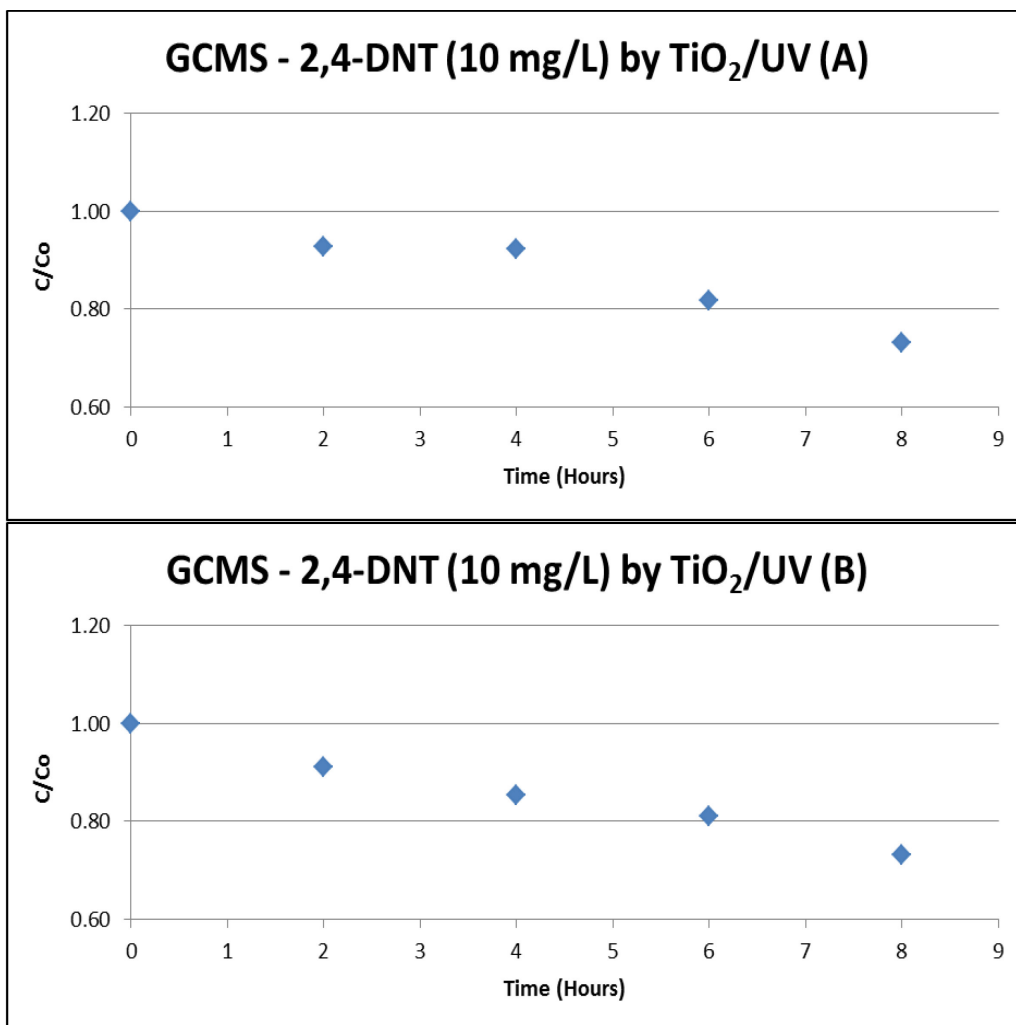
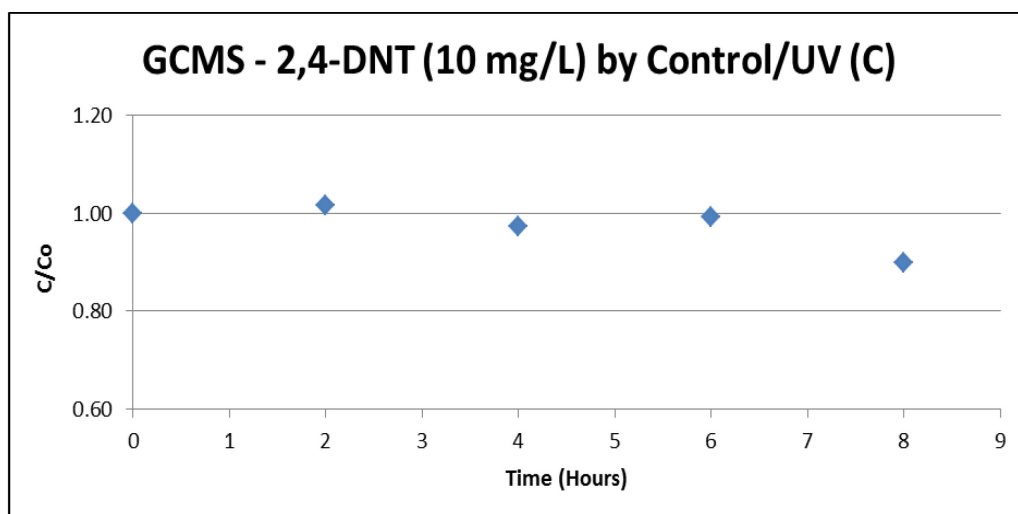
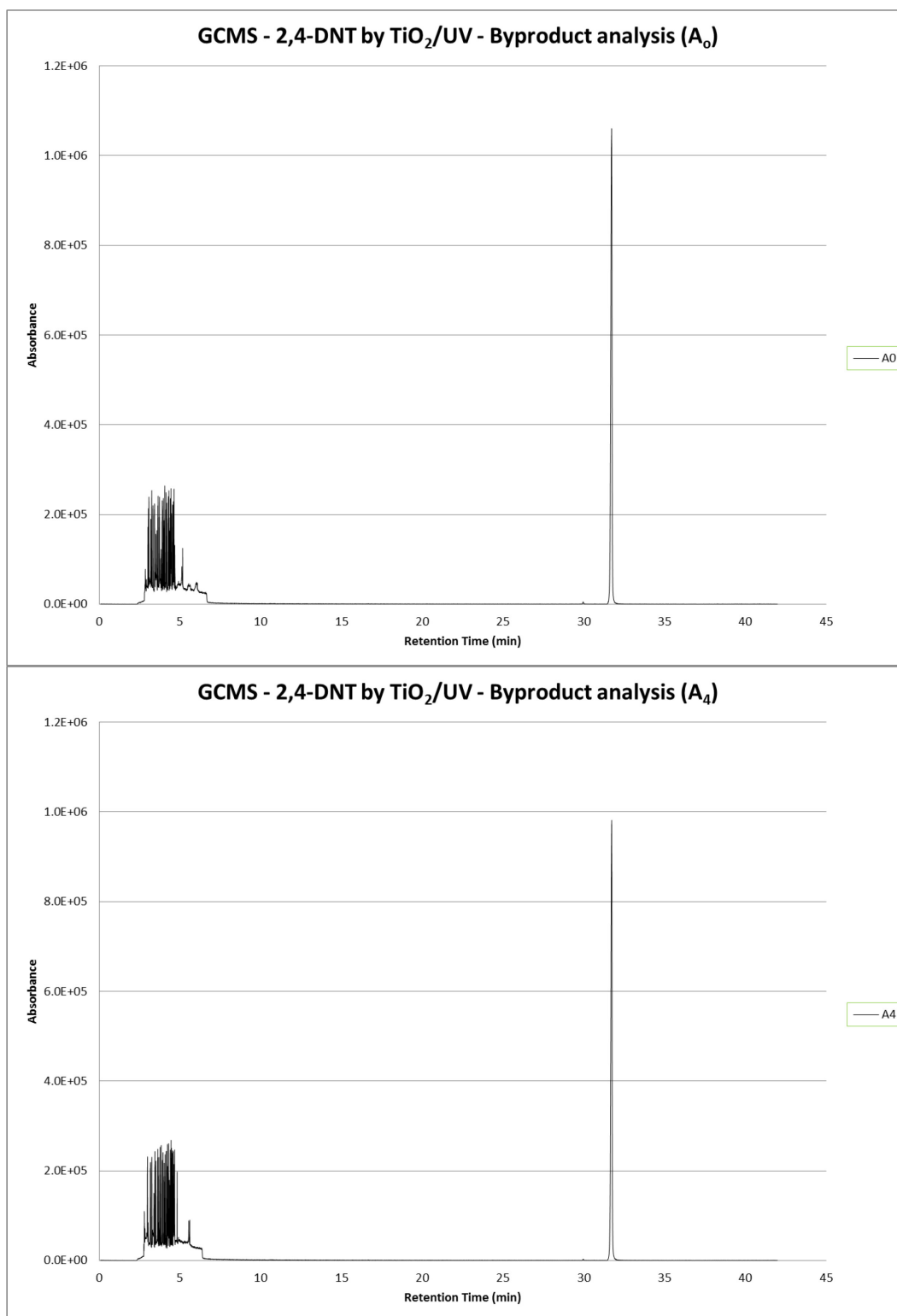


Figure 28 - GCMS experiment results (A) and (B) - 2,4-DNT ( $10 \text{ mg L}^{-1}$ ),  $TiO_2$ /UV light

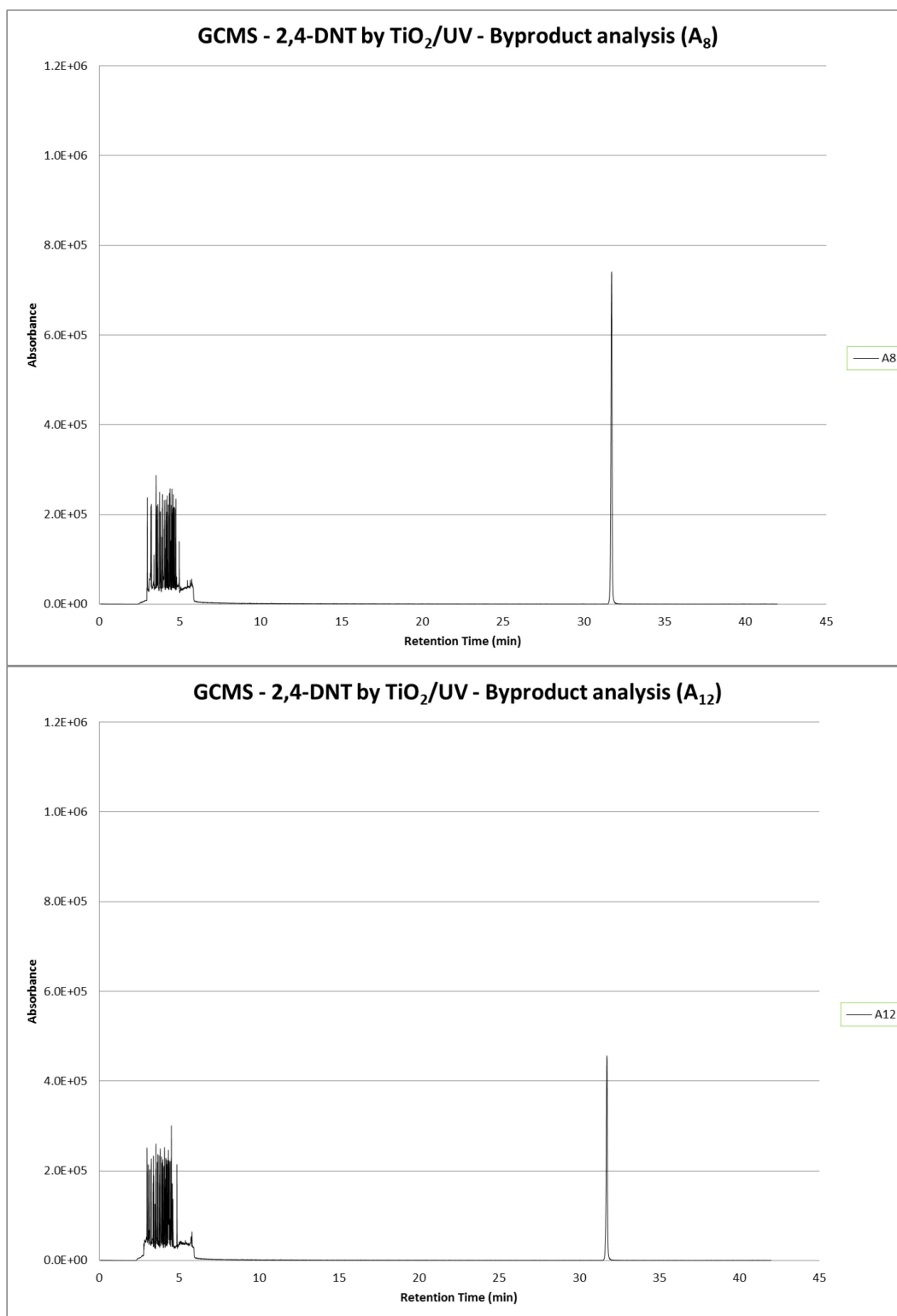


**Figure 29 - GCMS experiment results (C) - 2,4-DNT (10 mg L<sup>-1</sup>), Control/UV light**





**Figure 30 - GCMS experiment A results - 2,4-DNT (10 mg L<sup>-1</sup>), TiO<sub>2</sub>/UV light. (A<sub>0</sub>) Abundance profile at time 0 hrs, (A<sub>4</sub>) Abundance profile at time 4 hrs.**



**Figure 31 - GCMS experiment A results - 2,4-DNT (10 mg L<sup>-1</sup>), TiO<sub>2</sub>/UV light. (A<sub>8</sub>) Abundance profile at time 8 hrs, (A<sub>12</sub>) Abundance profile at time 12 hrs.**

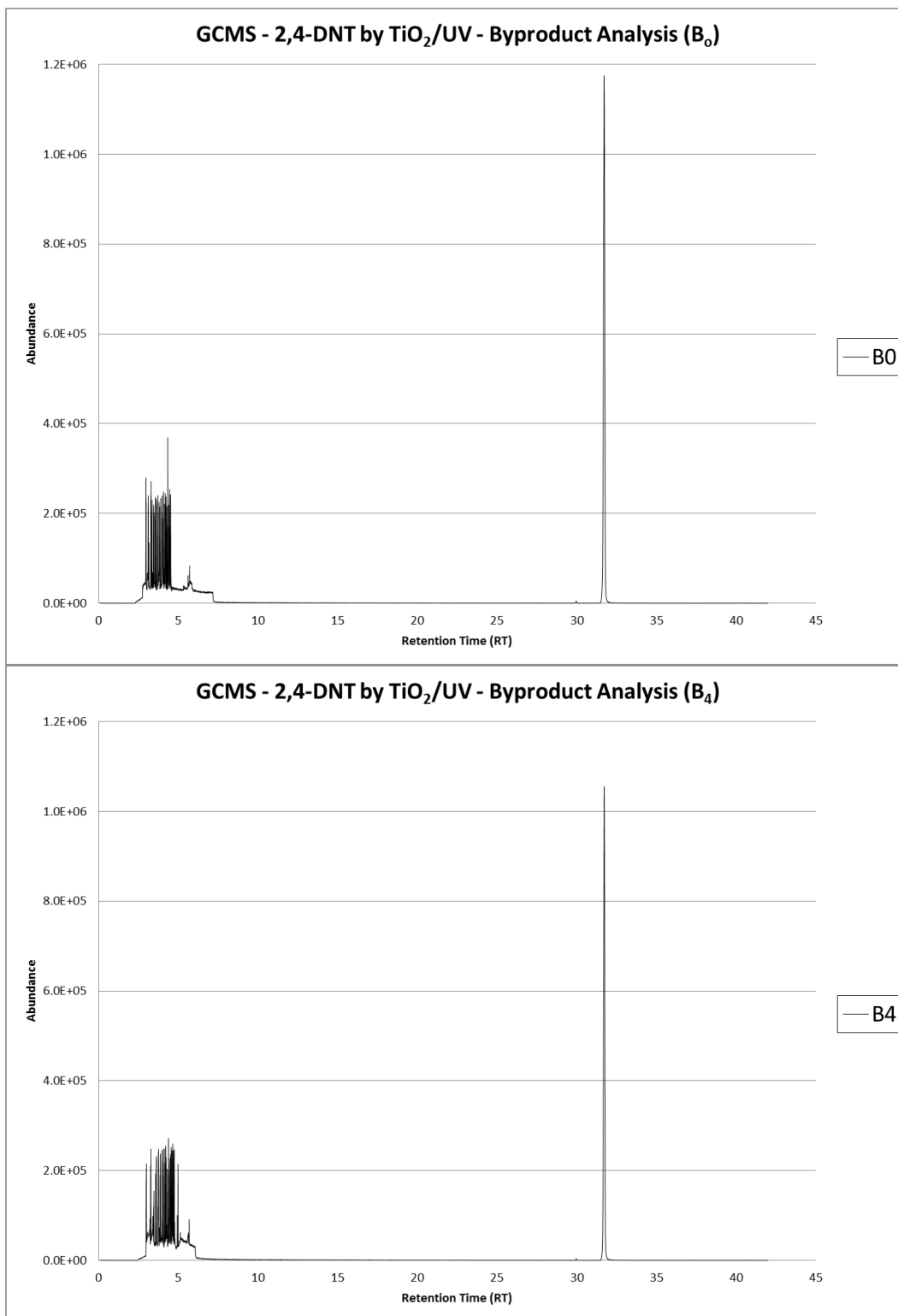
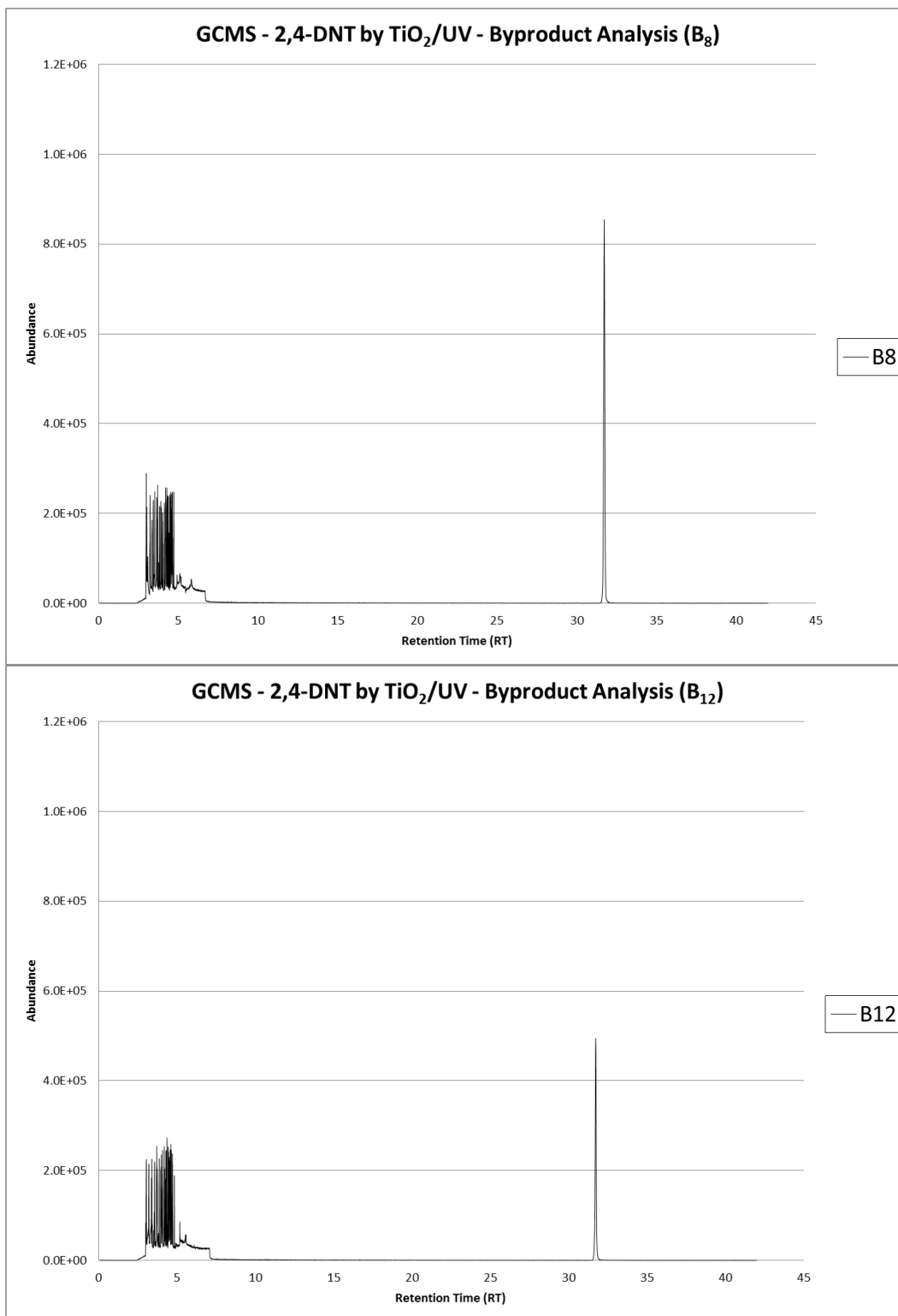


Figure 32 - GCMS experiment B results - 2,4-DNT ( $10 \text{ mg L}^{-1}$ ),  $\text{TiO}_2/\text{UV}$  light. (B<sub>0</sub>) Abundance profile at time 0 hrs, (B<sub>4</sub>) Abundance profile at time 4 hrs.



**Figure 33 - GCMS experiment B results - 2,4-DNT (10 mg L<sup>-1</sup>), TiO<sub>2</sub>/UV light. (B<sub>8</sub>) Abundance profile at time 8 hrs, (B<sub>12</sub>) Abundance profile at time 12 hrs.**

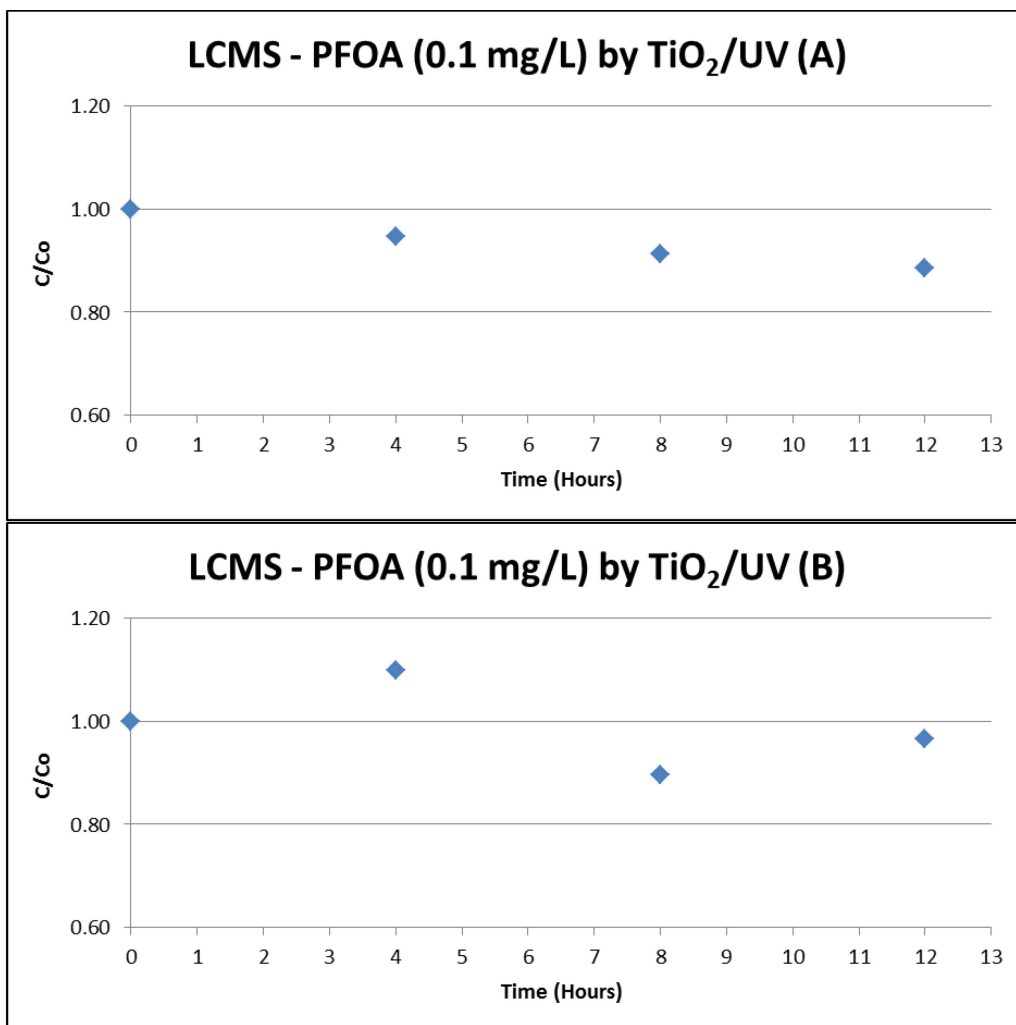


Figure 34 - LCMS experiment results (A) and (B) - PFOA (0.1 mg L<sup>-1</sup>), TiO<sub>2</sub>/UV light

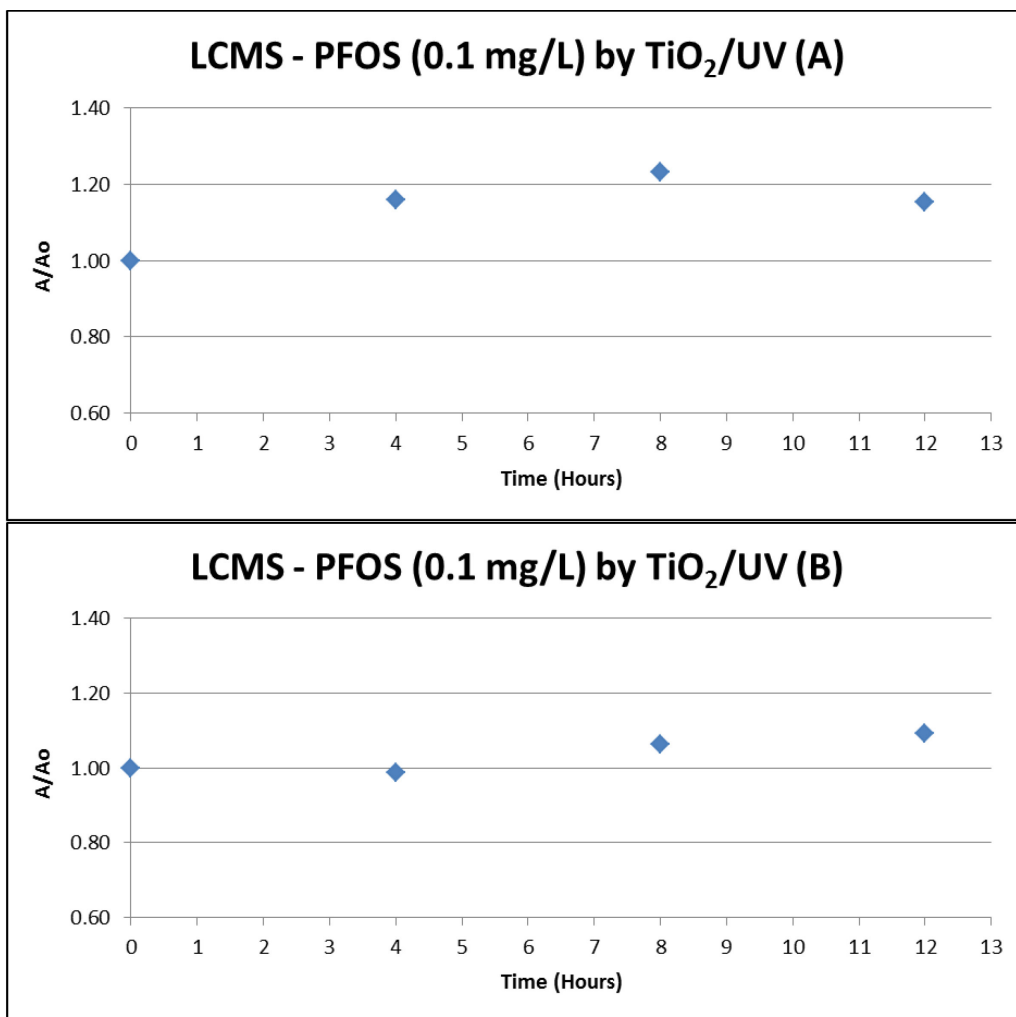


Figure 35 - LCMS experiment results (A) and (B) - PFOS (0.1 mg L<sup>-1</sup>), TiO<sub>2</sub>/UV light

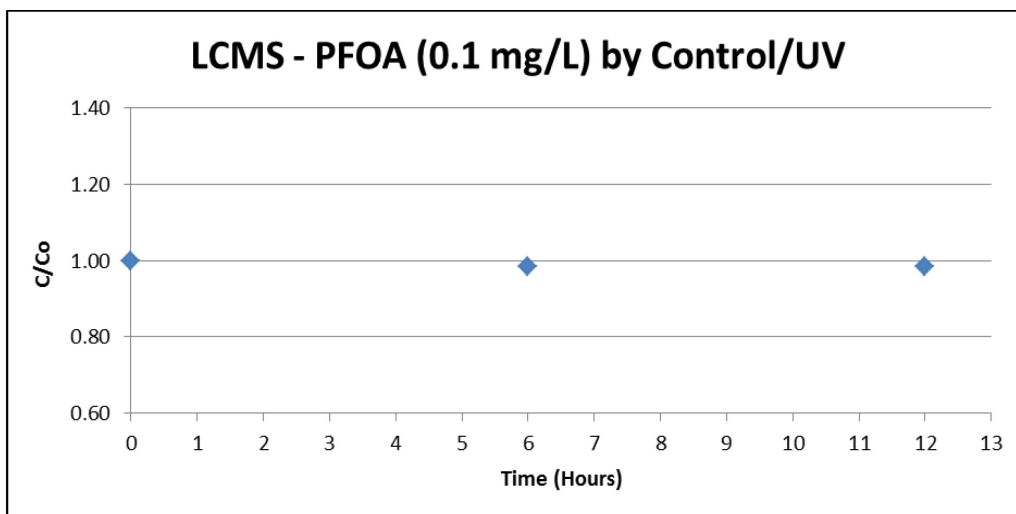


Figure 36 - LCMS experiment results - PFOA ( $0.1 \text{ mg L}^{-1}$ ), Control/UV light

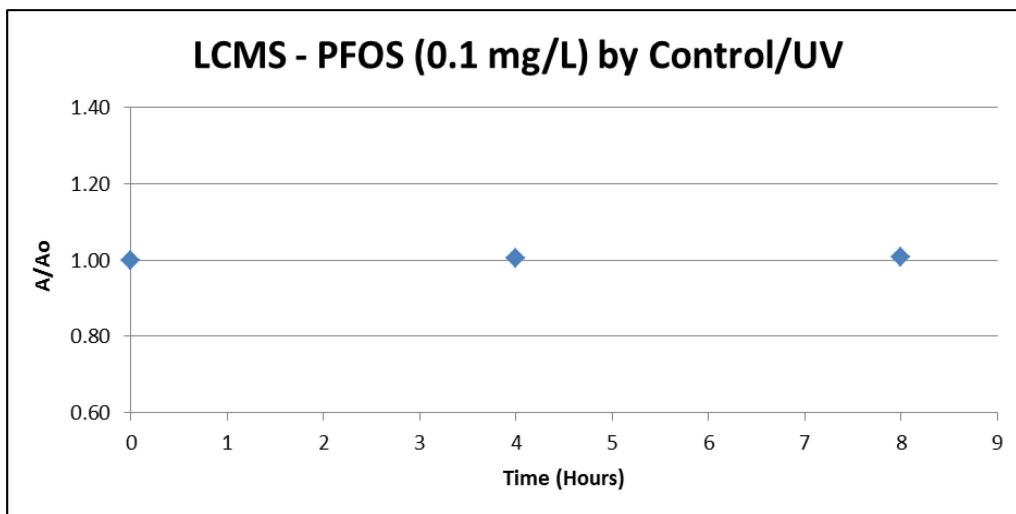


Figure 37 - LCMS experiment results - PFOS ( $0.1 \text{ mg L}^{-1}$ ), Control/UV light

## **Appendix B - Calibration Curves**



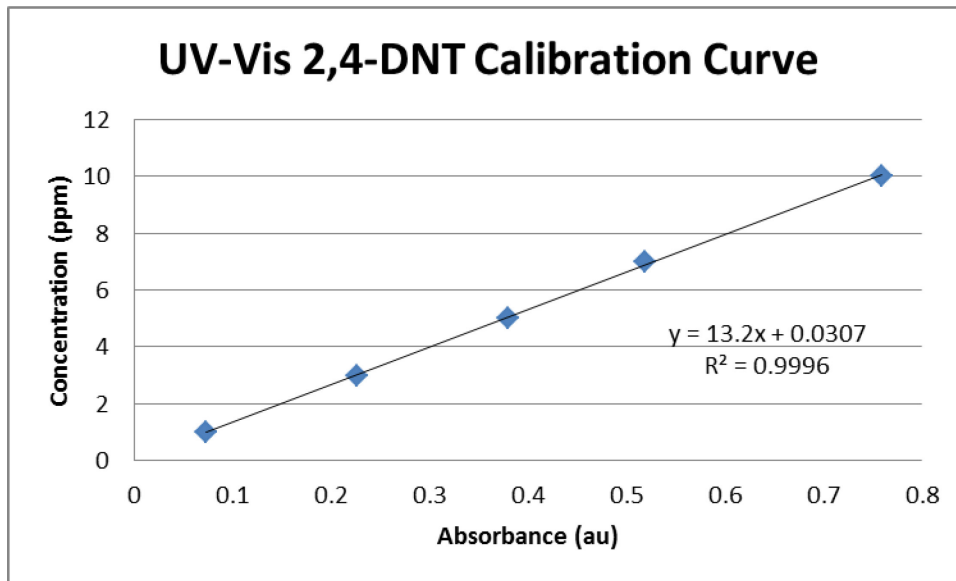


Figure 38 - UV-Vis 2,4-DNT Calibration Curve

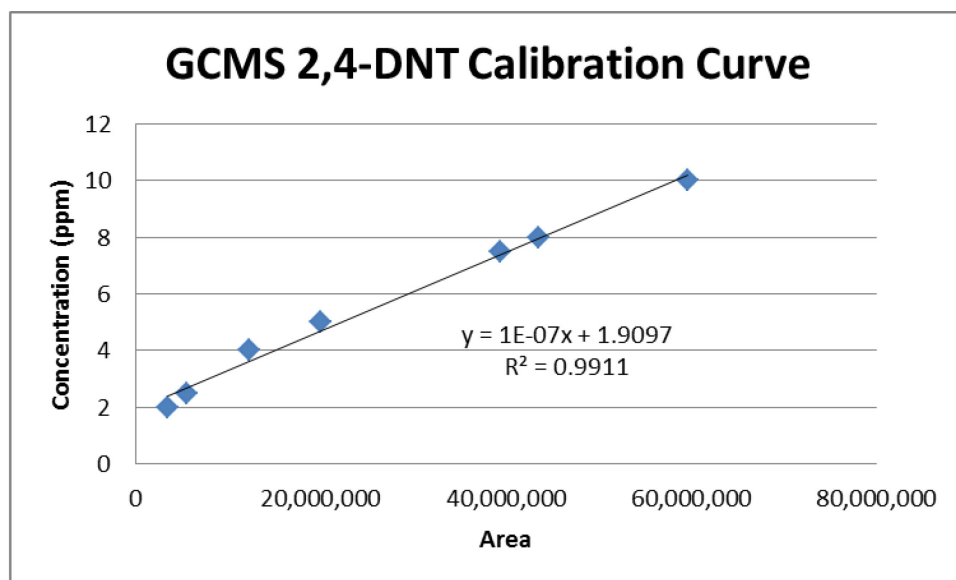
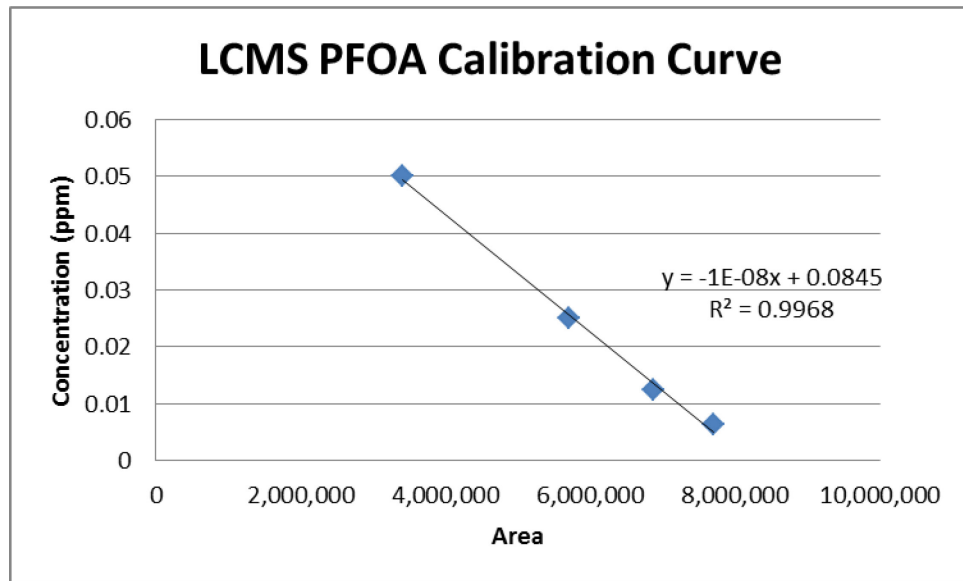


Figure 39 - GCMS 2,4-DNT Calibration Curve



**Figure 40 - LCMS PFOA Calibration Curve**

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## **Vita**

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14. ABSTRACT Nitroaromatic compounds (NACs) and perfluorinated compounds (PFCs) are two classes of water contaminants of DoD concern due to their risk to the environment, personnel, and mission. This study investigated the potential of an innovative technology, oxidation using titanium dioxide (TiO <sub>2</sub> ) and TiO <sub>2</sub> doped with silver (Ag-TiO <sub>2</sub> ) as photocatalysts, to effectively and energy efficiently treat NAC and PFC-contaminated water. Three model contaminants, 2,4-DNT (NAC), and PFOA and PFOS (PFCs), were degraded using TiO <sub>2</sub> and Ag-TiO <sub>2</sub> immobilized on glass slides under sunlight and UV light in atmospheric conditions and at neutral pH. 2,4-DNT degraded 14% and 15% in the presence of Ag-TiO <sub>2</sub> and TiO <sub>2</sub> , respectively, under sunlight after 8 hours. After 8 hours under UV light, 2,4-DNT degraded 13% and 29% in the presence of Ag-TiO <sub>2</sub> and TiO <sub>2</sub> , respectively. Results indicate that PFOA and PFOS do not degrade under the conditions of the experiment. Further study is needed to investigate the viability of the technology to treat NAC- and PFC-contaminated water.					
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